Contribution from the Dipartimento di Chimica Inorganica e Struttura Molecolare, Università di Messina, v. Sperone 31, I-98166 Vill. Sant'Agata, Messina, Italy

Synthesis, Absorption Spectra, and Luminescence Properties of Platinum(II) Complexes with Aminoquinoline and Aminoacridine Ligands

Luigi Monsù Scolaro,* Giuseppe Alibrandi, Raffaello Romeo, Vittorio Ricevuto, and Sebastiano Campagna*

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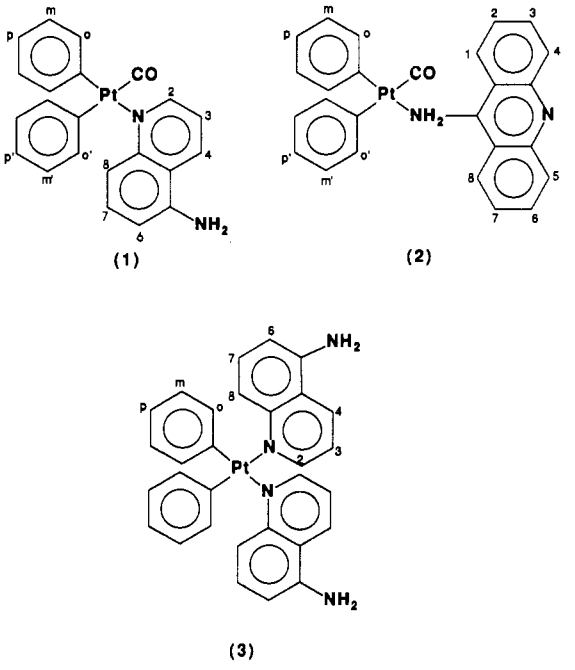
The synthesis, characterization, absorption spectra, and luminescence properties of three new platinum(II) complexes are reported. The complexes are $[Pt(C_6H_5)_2(CO)(5\text{-AQ})]$ (**1**), $[Pt(C_6H_5)_2(CO)(9\text{-AA})]$ (**2**), and $[Pt(C_6H_5)_2(5\text{-AQ})_2]$ (**3**) (5-AQ = 5-aminoquinoline; 9-AA = 9-aminoacridine). For the sake of comparison, the same properties of the 5-AQ and 9-AA free ligands have been studied. The absorption spectra of the complexes exhibit moderately intense bands (ϵ in the range 10^3–10^4 M^{-1} cm^{-1}) with maxima in the region 370–450 nm, which are assigned to π–π^* transitions centered in the N-heterocyclic ligands. The "Pt$(C_6H_5)_2$(CO)" and "Pt$(C_6H_5)_2$" moieties can be regarded as electron-withdrawing substituents of the aromatic ligands in that they substantially affect the energy of the bands by decreasing the π–π^* transition energies. All the complexes emit strongly both in fluid solution at room temperature (e.g., Φ = 0.037 for **2** in dichloromethane) and in a rigid matrix at 77 K. The emission bands are solvent dependent, with the emission energy decreasing on increasing solvent polarity, and the luminescence lifetimes are in the nanosecond range; the luminescence properties indicate that emission occurs from singlet π–π^* excited states centered in the N-heterocyclic aromatic ligands. Because of the nature of the heterocyclic amino-substituted ligands, and of the absorption and luminescence properties, these and similar complexes hold promise of being good luminescent probes for biological applications.

Introduction

In the last few years the design and the study of luminescent transition metal complexes have attracted much attention, because of the fundamental and applicative properties that such molecules are expected to exhibit. From a fundamental viewpoint, such species have played, and are still playing, important roles in the development of several branches of the chemistry, such as photochemistry, photophysics, chemiluminescence, electrochemiluminescence, and electron-transfer chemistry.[1-7] On the other side, luminescent metal complexes have been proposed to be useful, for example, for a number of solar energy conversion processes,[2,3,7-11] as labels for specific sites in polymeric arrays[12] and biological systems,[13,14] and more generally in microenvironmental research.[15]

In spite of the high number of d^6 transition metal complexes which exhibit room-temperature luminescence,[2,3,7,11] only few d^8 metal complexes are known to be emissive in fluid solution at room temperature. In particular, as far as platinum(II) complexes are concerned, recent work has reported emissions that originate from triplet metal-to-ligand charge-transfer (^{3}MLCT) excited states in cyclometalated complexes,[16] from triplet ligand-centered (^{3}LC) excited states[17] in complexes having high-energy ligand-field excited states, and from $d\sigma^*$ excited states in metal–metal-bonded polynuclear systems.[18] In a very few cases, excimer emission has

Chart I



(1) Lees, A. J. *Chem. Rev.* **1987**, *87*, 711.
(2) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85 and references therein.
(3) Meyer, T. J. *Acc. Chem. Res.* **1989**, *22*, 163.
(4) Watts, R. J. *Comments Inorg. Chem.* **1991**, *11*, 303. Nocera, D. G.; Maverick, A. W.; Winkler, J. R.; Che, C.-M.; Gray, H. B. In *Inorganic Chemistry: Toward the 21st Century*; Chisholm, M. H., Ed.; ACS Symposium Series 211; American Chemical Society: Washington, DC, 1983; p 21.
(5) Graetzel, M.; Ed.; *Energy Resources through Photochemistry and Catalysis*; Academic Press: London, 1983.
(6) Balzani, V.; Barigelletti, F.; De Cola, L. *Top. Curr. Chem.* **1990**, *158*, 31.
(7) Scandola, F.; Indelli, M. T.; Chiorboli, C.; Bignozzi, C. A. *Top. Curr. Chem.* **1990**, *158*, 73.
(8) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Horwood: Chichester, U.K., 1991.
(9) Fox, M. A., Chanon, M., Eds.; *Photoinduced Electron Transfer*; Elsevier: Amsterdam, 1988. Norris, J. M., Meisel, D., Eds.; *Photochemical Energy Conversion*; Elsevier: Amsterdam, 1989.
(10) Dabertani, R.; Bard, A. J.; Campion, A.; Fox, M. A.; Mallonk, T. E.; Webber, S. E.; White, J. M. *J. Phys. Chem.* **1988**, *92*, 1872. Vlachopulos, N.; Liska, P.; Augustynski, J.; Graetzel, M. *J. Am. Chem. Soc.* **1988**, *110*, 1216. Amadelli, R.; Argazzi, R.; Bignozzi, C. A.; Scandola, F. *J. Am. Chem. Soc.* **1990**, *112*, 7099.
(11) Denti, G.; Campagna, S.; Sabatino, L.; Serroni, S.; Ciano, M.; Balzani, V. In *Photochemical Conversion and Storage of Solar Energy*; Pelizzetti, E., Schiavello, M., Eds.; Kluwer: Dordrecht, The Netherlands, 1991; p 27.
(12) Kalyanasundaram, K. *Photochemical Processes in Microheterogeneous Systems*; Academic Press: New York, 1989.
(13) Tossi, A. B.; Kelly, J. M. *Photochem. Photobiol.* **1989**, *49*, 545.
(14) Pyle, A. M.; Rehmann, J. P.; Meshoyer, R.; Kumar, C. V.; Turro, N. J.; Barton, J. K. *J. Am. Chem. Soc.* **1988**, *111*, 3051.
(15) Masschelein, A.; Kirsch-De Mesmaeker, A.; Willsher, C. J.; Wilkinson, F. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 259.
(16) Maestri, M.; Sandrini, D.; Balzani, V.; Chassot, L.; Jolliet, P.; von Zelewsky, A. *Chem. Phys. Lett.* **1985**, *122*, 375. Barigelletti, F.; Sandrini, D.; Maestri, M.; Balzani, V.; von Zelewsky, A.; Chassot, L.; Jolliet, P.; Maeder, U. *Inorg. Chem.* **1988**, *27*, 3644. Balzani, V.; Maestri, M.; Deuchel-Cornioley, C.; von Zelewsky, A. *Adv. Photochem.*, in press.
(17) Sandrini, D.; Maestri, M.; Balzani, V.; Chassot, L.; von Zelewsky, A. *J. Am. Chem. Soc.* **1987**, *109*, 7720. Ballardini, R.; Gandolfi, M. T.; Prodi, L.; Ciano, M.; Balzani, V.; Kohnke, F. H.; Shariari-Zavareh, H.; Spencer, N.; Stoddart, J. F. *J. Am. Chem. Soc.* **1989**, *111*, 7072. Blanton, C. B.; Rillema, D. P. *Inorg. Chim. Acta* **1990**, *168*, 145. Wan, T. O.; Che, C. M. *J. Chem. Soc., Chem. Commun.* **1990**, 140.
(18) Rounhill, D. M.; Gray, H. B.; Che, C. M. *Acc. Chem. Res.* **1989**, *22*, 55. Shin, Y. K.; Miskowski, V. M.; Nocera, D. G. *Inorg. Chem.* **1990**, *29*, 2303.

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also been reported.[19] In most of these systems, a key role is surely played by the presence of a sufficiently high energy gap between the lowest (emitting) excited state(s) and upper lying metal-centered (MC) excited states, which are populated by thermal activation and deactivate the excited state by fast radiationless processes and/or photoreaction.[2,3] On the other hand, if the (emitting) excited-state energy is too low-lying, the rate of the radiationless processes increases, thereby preventing emission.

In this paper, we report the synthesis, characterization, absorption spectra, and luminescence properties of three new Pt(II) complexes containing amino-substituted N-heterocyclic ligands (Chart I), which are strongly luminescent in solution by themselves. The choice of other (nonchromophoric) ligands was dictated by the need to induce a high ligand-field strength to obtain a high-energy MC excited state.

Experimental Section

5-Aminoquinoline (5-AQ) and 9-aminoacridine (9-AA) hydrochlorides were purchased from Aldrich, and their purity was checked by NMR spectroscopy.

The solvents used were purified and dried before use by standard techniques. All the other chemicals were of the best commercial grade available. Infrared spectra were recorded in the range 4000–400 cm^{-1} using KBr cells, dichloromethane as solvent, and a Perkin-Elmer FT-IR Model 1730 spectrometer. One- and two-dimensional correlated (COSY) ^1H NMR spectra were recorded on a Bruker AMX-600 spectrometer operating at 600 MHz. Chemical shifts are reported in ppm (δ) from TMS as internal reference. ^{13}C NMR spectra were obtained on a Varian Gemini 300 spectrometer. ^{13}C NMR chemical shifts were taken with reference to the solvent peak and are reported in ppm versus TMS. All NMR spectra were obtained in acetone-d_6. Positive-ion FAB mass spectra were obtained in a glycerol matrix (GLI) by means of a Kratos MS 50S double-focusing mass spectrometer equipped with a standard FAB source.

The absorption spectra were recorded on a Kontron Uvikon 860 spectrophotometer. A Perkin-Elmer LS-5B spectrofluorimeter equipped with a Hamamatsu R928 phototube was used to obtain luminescence spectra. Luminescence lifetimes were measured with an Edinburgh single-photon-counting instrument, using a hydrogen discharge pulsed-light source (pulse width 2 ns); the emission decay traces were deconvoluted for the instrumental flash lamp by the Marquadt algorithm. For each measurement, at least five determinations were carried out. Experimental errors were <10%. Luminescence quantum yields were measured by the optical dilution method,[20] by using $Ru(bpy)_3^{2+}$ in aerated aqueous solution as the standard ($\Phi = 0.028$[21]); in these measurements the emission spectra were corrected for phototube response by a calibration lamp.

Preparation of Complexes. The 9-aminoacridine free base was prepared from its hydrochloride salt by neutralization with an excess of $NaHCO_3$ in water. After filtration, the compound was washed with several portions of water and purified by crystallization from ethanol.

***cis*-$[Pt(C_6H_5)_2(CO)(SEt_2)]$** was prepared by the literature method[22] and was crystallized from hexane.

***cis*-$[Pt(C_6H_5)_2(CO)(N1\text{-}5\text{-}AQ)]$ (1).** 5-Aminoquinoline (65 mg, 0.45 mmol) and *cis*-$[Pt(C_6H_5)_2(CO)(SEt_2)]$ (200 mg, 0.43 mmol) were reacted in dichloromethane (50 mL) with stirring in the dark. The progress of the reaction was monitored by TLC on Al_2O_3. After completion of the reaction, the dark yellow solution was concentrated under reduced pressure. The complex was precipitated as fine yellow needles by slow addition of hexane, giving 170 mg of a crude product. Recrystallization from a 1:2 dichloromethane/hexane mixture gave 150 mg of pure product (yield 67%).

IR: ν(C=O) 2065 cm^{-1}. ^1H NMR: δ 9.29 (d, ^3J = 4.98 Hz, $^3J_{Pt-H}$ = 25.2 Hz, 1 H), 8.95 (d, ^3J = 8.53 Hz, 1 H), 8.82 (d, ^3J = 8.48 Hz, 1 H), 7.94 (t, av ^3J = 7.97 Hz, 1 H), 7.65 (q, ^3J = 4.98 Hz, ^3J = 8.53 Hz, 1 H), 7.63 (d, ^3J = 6.74 Hz, $^3J_{Pt-H}$ = 77.45 Hz, 2 H), 7.24 (d, ^3J = 8.13 Hz, $^3J_{Pt-H}$ = 60.43 Hz, 2 H), 7.16 (d, ^3J = 7.72 Hz, 1 H), 7.09 (t, av ^3J = 7.62 Hz, 2 H), 6.99 (t, av ^3J = 7.26 Hz, 1 H), 6.90 (t, av ^3J = 7.67 Hz, 2 H), 6.78 (t, av ^3J = 7.27 Hz, 1 H), 6.00 (br s, 2 H). ^{13}C NMR: δ(CO) 181. FABMS (GLI) *m/e*: 613, $[M + GLI]^+$; 521, $[M]^+$ (matches theoretical isotope distribution); 493, $[M - CO]^+$; 349, $[M - CO - 5\text{-}AQ]^+$; 145, $[5\text{-}AQ + H^+]^+$. Anal. Calcd for $C_{22}H_{18}ON_2Pt$: C, 50.67; H, 3.47; N, 5.37. Found: C, 50.58; H, 3.40; N, 5.41.

***cis*-$[Pt(C_6H_5)_2(CO)(N9\text{-}9\text{-}AA)]$ (2).** 9-Aminoacridine (90 mg, 0.46 mmol) was reacted with *cis*-$[Pt(C_6H_5)_2(CO)(SEt_2)]$ (200 mg, 0.43 mmol) in dichloromethane (100 mL) in the dark under stirring. The reaction was complete in 2 days, as evidenced by TLC on Al_2O_3. The orange solution was evaporated to a small volume under reduced pressure, and the compound was precipitated by slow addition of hexane (200 mg, yield 81.5%). Crystallization from dichloromethane/hexane (1:2) gave 170 mg of bright orange crystals (yield 69.2%).

IR: ν(C=O) 2062 cm^{-1}. ^1H NMR: δ 9.86 (d, ^3J = 8.83 Hz, 2 H), 8.62 (d, ^3J = 9.17 Hz, 2 H), 8.17 (br s, 2 H), 8.15 (t, av ^3J = 7.75 Hz, 2 H), 7.77 (d, ^3J = 8.41 Hz, $^3J_{Pt-H}$ = 76.33 Hz, 2 H), 7.63 (t, av ^3J = 7.62 Hz, 2 H), 7.24 (d, ^3J = 8.14 Hz, $^3J_{Pt-H}$ = 59.92 Hz, 2 H), 7.14 (t, av ^3J = 7.35 Hz, 2 H), 7.02 (t, av ^3J = 7.27 Hz, 1 H), 6.77 (t, av ^3J = 7.34 Hz, 2 H), 6.68 (t, av ^3J = 7.26 Hz, 1 H). ^{13}C NMR: δ(CO) 181. FABMS (GLI) *m/e*: 571, $[M]^+$; 543, $[M - CO]^+$; 195, $[9\text{-}AA + H^+]^+$. Anal. Calcd for $C_{26}H_{20}ON_2Pt$: C, 54.64; H, 3.52; N, 4.90. Found: C, 54.70; H, 3.42; N, 4.72.

A further purification of compounds **1** and **2**, as necessary for the photochemical studies, was obtained by column chromatography over Al_2O_3 using dichloromethane as eluent.

***cis*-$[Pt(C_6H_5)_2(N1\text{-}5\text{-}AQ)_2]$ (3).** 5-Aminoquinoline (120 mg, 0.8 mmol) was allowed to react with $[Pt(C_6H_5)_2(\mu\text{-}SEt_2)]_2$ (176 mg, 0.2 mmol) in 50 mL of dichloromethane with stirring. After 36 h, the reaction mixture deposited a fine yellow-green precipitate, which was collected and washed with a few portions of cold dichloromethane. The compound was purified by several recrystallizations from CH_2Cl_2/hexane (64 mg, yield 25%).

^1H NMR: δ 9.42 (d, ^2J = 4.94 Hz, 2 H), 9.34 (d, ^2J = 6.04 Hz, 2 H), 8.47 (d, ^2J = 8.66 Hz, 2 H), 7.59 (t, av ^2J = 8.25 Hz, 2 H), 7.32 (d, ^2J = 7.14 Hz, $^3J_{Pt-H}$ = 76.86 Hz, 4 H), 7.25 (q, av ^2J = 8.54 Hz, 2 H), 6.78 (d, ^2J = 7.64 Hz, 2 H), 6.59 (t, av ^2J = 7.14 Hz, 4 H), 6.53 (t, av ^2J = 6.60 Hz, 2 H), 5.49 (br s, 4 H). FABMS (GLI) *m/e*: 638, $[M]^+$; 493, $[M - 5\text{-}AQ]^+$; 145, $[5\text{-}AQ + H^+]^+$. Anal. Calcd for $C_{30}H_{26}N_4Pt$: C, 56.50; H, 4.11; N, 8.78. Found: C, 56.35; H, 4.02; N, 8.80.

Results

Under the conditions indicated in the Experimental Section, the displacement of the coordinated thioether from the complex *cis*-$[Pt(C_6H_5)_2(CO)(SEt_2)]$ takes place readily and there is no sign of removal of carbon monoxide. Thus, complexes **1** and **2** were prepared according to the reaction

$$cis\text{-}[Pt(C_6H_5)_2(CO)(SEt_2)] + L \rightarrow cis\text{-}[Pt(C_6H_5)_2(CO)(L)] + SEt_2 \quad (1)$$

and complex **3** was prepared by the bridge-splitting reaction

$$[Pt(C_6H_5)_2(\mu\text{-}SEt_2)]_2 + 4L \rightarrow 2cis\text{-}[Pt(C_6H_5)_2(L)_2] + 2SEt_2 \quad (2)$$

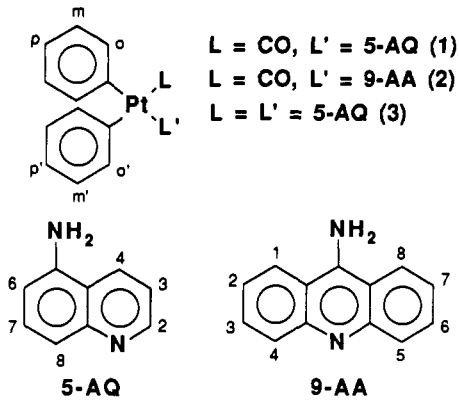
The detection by TLC of an intermediate product, tentatively assigned to the monosubstituted species, indicates that the latter process takes place in two consecutive steps, but at the end of the reaction, only species **3** was isolated from the reaction mixture.

^1H NMR assignments for 5-aminoquinoline and 9-aminoacridine were verified by standard NMR techniques. The assignment of the ^1H NMR peaks of compound **1** was facilitated by the large coupling constants due to the 33.8% abundant ^{195}Pt isotope with $I = {}^1/_2$. Thus, the signal at 9.29 ppm, which is downfield-shifted with respect to that of the free ligand (0.4 ppm) and shows two ^{195}Pt satellites, is assigned to the H2 proton of the quinoline ring. The H8 proton resonance is even more largely downfield-shifted with respect to the signal of the free ligand (1.31 ppm). The remaining proton resonances of the quinoline ring were assigned on the basis of their connectivity in the COSY spectra. The resonances of the phenyl rings were assigned on the basis of their coupling constants, ^{195}Pt chemical shifts, and connectivity in the COSY spectra.

The ^1H NMR spectrum of compound **2** was interpreted by assigning the resonance at 9.86 ppm to the H1,8 protons of the acridine ring and by assigning the remaining signals on the basis of their connectivity in the COSY spectra and their ^{195}Pt coupling constants. The ^1H NMR spectrum of compound **3** was assigned according to the coupling pattern of the quinoline ligand and the connectivity in the COSY spectrum.

(19) Kunkely, H.; Vogler, A. *J. Am. Chem. Soc.* **1990**, *112*, 5625. Wan, K. T.; Che, C. M.; Cho, K. C. *J. Chem. Soc., Dalton Trans.* **1991**, 1077.
(20) Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991.
(21) Nakamura, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2697.
(22) Steele, B. R.; Vrieze, K. *Transition Met. Chem.* **1977**, *2*, 140.

Table I. ^{1}H NMR Data for Complexes 1–3



proton	δ^a compd 1	δ^a compd 3	proton	δ^a compd 2
H2	9.29 (+0.40)^b	9.42 (+0.55)	H1,8	9.86 (+1.37)^b
H3	7.65 (+0.30)	7.25 (−0.10)	H2,7	8.15 (+0.34)
H4	8.95 (+0.77)	8.47 (+0.29)	H3,6	7.63 (+0.14)
H6	7.16 (+0.35)	6.78 (−0.03)	H4,5	8.62 (+0.55)
H7	7.94 (+0.37)	7.59 (+0.08)	Ho	7.77
H8	8.82 (+1.31)	9.34 (+1.77)	Hm	7.14
Ho	7.63	7.32	Hp	7.02
Hm	7.09	6.59	Ho′	7.24
Hp	6.99	6.53	Hm′	6.77
Ho′	7.24		Hp′	6.68
Hm′	6.90		NH_2	8.17 (+0.81)
Hp′	6.78			
NH_2	6.00 (+0.05)	5.49 (−0.46)		

^{a}Chemical shift in ppm. ^{b}In parentheses is reported the difference relative to the free ligand. A positive value indicates a downfield shift.

Detailed ^{1}H NMR assignments for compounds 1–3 are reported in Table I.

All the complexes, as well as the free ligands, are fairly stable in dichloromethane (DCM) and acetone solutions at least for 24 h, as shown by the constancy of their absorption spectra. On the contrary, 1 and 3 exhibit a slight thermal reactivity in acetonitrile (AN) within 2 h after dissolution, most likely due to removal of the quinoline ligand(s) by solvolysis. The same behavior was also exhibited in alcoholic solvents. For this reason, all experiments were performed on freshly prepared samples.

The electronic absorption spectra of all the complexes show a strong absorption band with a maximum at $\lambda < 270$ nm (ϵ 10^4–10^5 M^{-1} cm^{-1}) and a moderately intense band in the near-UV or visible region (ϵ 10^3–10^4 M^{-1} cm^{-1}). When DCM is replaced by AN, the maximum of the lowest energy band moves to lower energies. The absorption spectra of the 5-AQ and 9-AA free ligands exhibit absorption bands in the same energy region of the spectrum, but with the maximum blue-shifted with respect to the relative complexes. The same solvent dependence observed for the absorption bands of the complexes is also displayed by the absorption bands of the free ligands (Table II).

All the complexes exhibit luminescence both in fluid solution at room temperature and in a rigid matrix at 77 K; the shape of the emission is structureless for the quinoline complexes 1 and 3, whereas the typical shape of anthracene derivative emission[23]

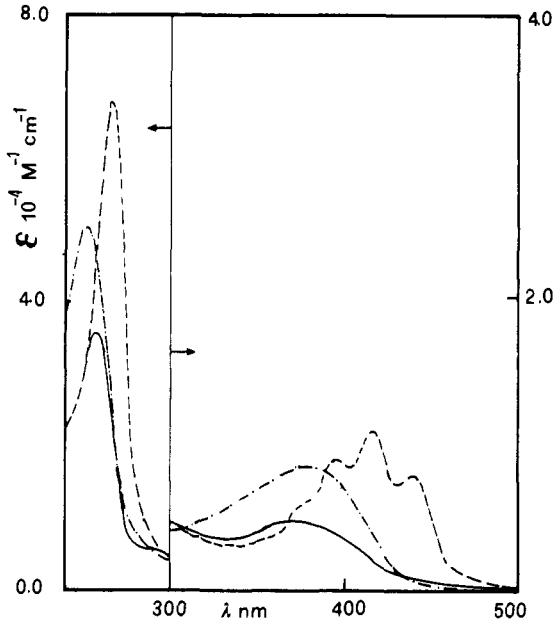


Figure 1. Absorption spectra of 1 (—), 2 (- - -), and 3 (-·-) in dichloromethane solution.

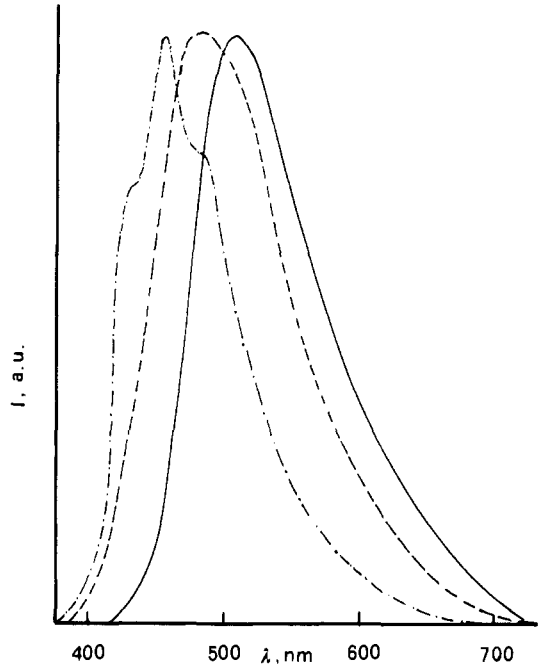


Figure 2. Emission spectra of 1 (—), 2 (-·-), and 3 (- - -) in acetonitrile solution.

Table II. Absorption and Luminescence Data^a

	absorption, 298 K		luminescence, 298 K			luminescence, 77 K
	DCM	AN	DCM		AN	BN
	λ_{max}, nm (ϵ, M^{-1} cm^{-1})	λ_{max}, nm	λ_{max}, nm (τ, ns)	Φ	λ_{max}, nm (τ, ns)	λ_{max}, nm (τ, ns)
$[Pt(C_6H_5)_2(CO)(5\text{-AQ})]$ (1)	377 (4500)	385	504 (4)	0.024	530 (12)	485 (5)
$[Pt(C_6H_5)_2(CO)(9\text{-AA})]$ (2)	439 (11 000)	443	482 (3)	0.037	485 (6)	482 (7)
$[Pt(C_6H_5)_2(5\text{-AQ})_2]$ (3)	379 (8800)	380	460 (19)	0.002	492 (12)	462 (25)
5-AQ	350	356	455	0.073	475	
9-AA	420	421	460		462	

^{a}Abbreviations: DCM = dichloromethane, AN = acetonitrile; BN = butyronitrile. For the absorption spectra, λ_{max} refers to the lowest energy maximum.

is apparent in the spectrum of the 9-AA complex **2**. Once again, the maximum of the emission shifts to the red on passing from the free ligands to the complexes and from DCM to AN solutions. The luminescence lifetimes are in the nanosecond range and do not change substantially with temperature. Table II collects the absorption and luminescence data, Figure 1 shows the absorption spectra of the complexes in DCM, and Figure 2 shows the emission spectra of the three complexes in AN solution at room temperature. Corrected excitation spectra have been obtained for the three complexes in all the solvents used and have been found to closely match the respective absorption spectra.

Discussion

Synthesis and NMR Spectra. 5-Aminoquinoline possesses two nitrogen atoms which can act as donor sites with regard to platinum(II). On the basis of its basicity, the endocyclic nitrogen N1 is expected to be the donor atom, and indeed, as evidenced by ^{1}H NMR spectra, 5-aminoquinoline binds to platinum(II) through this atom. The most important feature in the NMR spectra of **1** and **3** is the downfield shift of the H2 and H8 resonances, strongly indicative of coordination through N1. The H2 hydrogen in **1** and the ortho hydrogens on the aromatic phenyl rings in **1** and **3** show the presence of ^{195}Pt coupling. The H2 resonance of compound **1**, in particular, exhibits a broadening of the ^{195}Pt satellites, due to a chemical shift anisotropy relaxation mechanism,[25a] which becomes more evident on going from the 300-MHz to the 600-MHz spectra. Upon coordination, H8 is deshielded to a greater extent than H2 in both complexes, probably due to the proximity of this proton to the metal center, as shown by CPK models. Since, for some sterically hindered ligands, a short nonbonded metal–proton contact had led to an agostic interaction,[25b] we examined the systems and verified that there was no agostic interaction for this proton. This is probably the result of a low-energy barrier and of a rapid rotation around the Pt–N1 bond.

It is worthy of note that Sundquist, Bancroft, and Lippard, for the strictly similar complex *cis*-$[Pt(NH_3)_2(N1\text{-}HCQ)Cl]^+$ (HCQ = chloroquine),[26] have shown the presence of two different diastereoisomers, resulting from the hindrance of the HCQ ligand, which is in a rigid position around the Pt–N1 bond. In our case, the quinoline ring is remarkably less crowded than the chloroquine and its rotation around the Pt–N1 bond much easier, although the phenyl rings play an important role in the total steric environment.

9-Aminoacridine derives from a class of very important molecules that have remarkable biological activity, as they interact with nucleic acid by an intercalative mechanism.[27] This molecule possesses two different binding sites for metals with very different basicities.[28a] The endocyclic nitrogen has a pK_a of 9.99, and it is expected to react with the soft platinum(II) center, but as recently reported in the literature,[26] platinum(II) coordinates preferentially to the amino group for steric reasons. Aminoacridine in solution can assume different tautomeric forms, but the amino form is preferred in organic solvents.[28b] The stabilization of an unusual imino tautomeric form of 9-aminoacridine upon platinum(II) coordination, which raises the resonance of each proton, has been recently reported[26] and thought to be due to the blocked rotation around the Pt–N9 bond. In contrast, in compound **2**, the presence of a single set of signals for the proton pairs H1,8, H2,7, H3,6, and H4,5 is in agreement with coordination through an sp^3 nitrogen atom and with rapid rotation, on the NMR time scale, of the acridine moiety around the Pt–N9 bond. The H1,8 proton resonances experience a remarkable downfield shift (1.37 ppm) due to the close contact with the metal center. An important feature of the spectrum of this complex is the temperature, solvent, and concentration dependence of the chemical shifts. This behavior is typical for free 9-aminoacridine and is indicative of the existence in solution of stacking interactions. Further studies are in progress to elucidate the possible biological implication of stacking interactions of such planar molecules, and the results of their use as intercalators with DNA will be reported elsewhere.

Absorption Spectra. The amino-substituted N-heterocyclic ligands used in this work present an extended aromaticity, and as a consequence, $\pi-\pi^*$ transitions are expected to occur at relatively low energy. Thus, the intense absorption bands in the near-UV region exhibited by the two free ligands can be confidently assigned to such $\pi-\pi^*$ transitions. The energy of the band maximum of 5-AQ shows a red shift with increasing polarity of the solvent (Table II). This fact is strongly indicative of a greater polarity of the $\pi-\pi^*$ excited state with respect to the ground state. As a consequence, a partial charge-transfer (CT) character can be attributed to the $\pi-\pi^*$ excited state of 5-AQ.

For the complexes, the low-energy maximum is also assigned to $\pi-\pi^*$ transitions within the 5-AQ and 9-AA aromatic ligands (ligand-centered (LC) transitions): arguments based on extinction coefficients, energy, and solvent dependence of the bands are in full agreement with this assignment.[17] As one can see from the data in Table II, the band is substantially red-shifted in the spectra of the complexes compared to that of the free ligands (e.g., 1100 cm^{-1} for complex **1** in DCM). The same effect occurs on protonation or in the presence of electron-withdrawing substituents on the N-heterocyclic ring. This pattern of behavior leads us to think that in these compounds the "Pt" moieties behave as electron acceptors, essentially through the σ-bonding framework. The electron-withdrawing ability of the "Pt" groups stabilizes the orbitals of the aromatic ligands, operating more effectively on the more polarizable π^* orbital.[29] Therefore, a decreased energy gap between the π and π^* orbitals involved in the LC transition is expected in the complexes compared to the free ligands, which accounts for the red shift of the band maximum.[17]

Platinum(II) complexes usually exhibit strong mixing between metal and ligand orbitals through a transfer of electronic density from occupied d orbitals of the metal to suitable vacant orbitals of the ligands.[30] The extent of this transfer toward a particular ligand is dictated by the presence in the coordination sphere of the metal of other "noninnocent" ligands, which are capable of competing for the same process. In these particular complexes, the contemporary presence of the good π-acceptor carbonyl group and of the phenyl ligands is expected to reduce markedly the amount of electron donation from the platinum d orbitals to the 5-AQ and 9-AA ligands. The possibility of electron donation from Pt d orbitals to π^* orbitals of 9-AA is further prevented in complex **2** because of the presence of the NH_2 "spacer". As far as the 5-AQ complexes are concerned, a detailed description of the extent of backbonding requires a theoretical approach, even though the experimental evidence at the hand (see also luminescence section) leads us to conclude that metal-centered and ligand-centered orbitals are not efficiently mixed.

Luminescence Properties. For both free ligands and complexes, the strong luminescence is attributed to the singlet lowest lying $\pi-\pi^*$ excited state centered on 5-AQ or 9-AA ligands. This assignment is based on (i) the overlap between absorption and emission spectra (Figures 1 and 2), (ii) the short luminescence lifetime (see Table II), (iii) the red shift of the complexes' emissions with respect to those of the free ligands, and (iv) the

(23) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin: Menlo Park, CA, 1983; Chapter 5.
(24) Ismail, I. M.; Kerrison, S. J. S.; Sadler, P. J. *Polyhedron* **1982**, *1*, 57. Lallemand, J.; Soulié, J.; Chottard, J. C. *J. Chem. Soc., Chem. Commun.* **1980**, 436.
(25) (a) Albinati, A.; Pregosin, P. S.; Wombacher, F. *Inorg. Chem.* **1990**, *29*, 1812. Albinati, A.; Anklin, C. G.; Ganazzoli, F.; Ruegg, H.; Pregosin, P. S. *Inorg. Chem.* **1987**, *26*, 503. (b) Reviews: Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395. Brookhart, M.; Green, M. L. H.; Wong, L. L. *Prog. Inorg. Chem.* **1988**, *36*, 1.
(26) Sundquist, W. I.; Bancroft, D. P.; Lippard, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 1590.
(27) Lerman, L. S. *J. Mol. Biol.* **1961**, *3*, 18.
(28) (a) Acheson, R. M. In *Heterocyclic Compounds*, 2nd ed.; Acheson, R. M., Ed.; Wiley: New York, 1973; Vol. 9, p 110. (b) *Ibid.*, p 121.
(29) Giannetto, A.; Guglielmo, G.; Giuffrida, A.; Ricevuto, V.; Campagna, S. *J. Photochem. Photobiol., A* **1990**, *53*, 23.
(30) (a) Hartley, F. G. In *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Stone, F. G. A.; Abel, E. W., Eds.; Pergamon Press: London, 1982; Vol. 6, p 471. (b) Tsipis, C. A. *Coord. Chem. Rev.* **1991**, *108*, 163. (c) Veillard, A. *Chem. Rev.* **1991**, *91*, 743.

solvent sensitivity of the emission maximum of the 5-AQ-containing compounds, in agreement with the charge-transfer character of the LC excited state in this ligand. Metal-centered excited states are not considered to be involved in the luminescence process. Actually, in spite of the presence of the heavy atom, the intersystem crossing from singlet to triplet $\pi-\pi^*$ excited states is not active in these Pt(II) complexes, thus making the luminescence properties of such compounds qualitatively different from those of other Pt(II) complexes which are also ligand-centered emitters.[17] The absence of the usual heavy-atom effect provides further confirmation for poor metal–ligand orbital mixing in these systems.

The luminescence solvent dependence of the emission maximum is greater than the absorption solvent dependence (see Table II) because of repolarization effects in the excited state before emission occurs: such effects enhance the ability of the solvent polarity to stabilize the (more polar) excited state. The difference in the red shift of the emission band of **1** and **3** with respect to the 5-AQ free ligand emission (55 nm vs 17 nm in acetonitrile solution at 298 K; see Table II) is in full agreement with our expectations because the electron-withdrawing ability of the "$Pt(C_6H_5)_2(CO)$" moiety is much stronger than that of "$Pt(C_6H_5)_2$" and affects the energy of the $\pi-\pi^*$ transition more substantially. Once again, **2** seems to be less sensitive to solvent polarity than **1** and **3**, as was the case for the absorption spectra. The purer LC nature of the $\pi-\pi^*$ transition in **2** with respect to **1** and **3** would account for such behavior.

As far as the low-temperature emission is concerned, the typical blue shift in emission maxima for charge-transfer emission on decreasing temperature[2] is exhibited by **1** and **3**, whereas the energy of the emission spectrum of **2** is practically unaffected, which confirms a less pronounced CT character for the $\pi-\pi^*$ transition in **2**. The structured shape of the luminescence spectrum of **2**, both at room temperature and at 77 K, further supports this conclusion.

As one can see from the data in Table II, the luminescence quantum yield of **3** is about 10 times lower than that of **1**, in spite of the fact that in both complexes emission comes from the same ligand and the same type of excited state. This behavior is likely due to the small energy gap between the emitting level and a closely lying MC excited state in **3**, which allows a fast radiationless decay. Actually, the replacement of a CO group by a quinoline ligand on passing from **1** to **3** is expected to decrease the ligand-field strength experienced by the metal and, as a consequence, also the energy of the MC excited state. The contemporary increase in energy of the emitting LC excited state further contributes to such an effect.

The luminescence quantum yields of the complexes (except for **3**) are not far from the values measured for the free ligands (compare the data for the 5-AQ compounds in Table II); this is a consequence of the fact that in these complexes the Pt ions are not heavily involved in the deactivation processes, but only affect the spectral properties of the free ligands. Such a property could make these species useful in the design of amino-substituted N-heterocyclic laser dyes,[31] in which a red shift of the emission spectrum is mainly required. Actually, the strong absorption of the $\pi-\pi^*$ bands, the relatively high luminescence quantum yields, the acceptable overlap between absorption and emission spectra, and the good solubility and thermal stability in acetone solution exhibited by the studied complexes are promising properties in this area. However, other lasing properties (in particular, photochemical stability) should be controlled and could pose problems.

Conclusions

The new Pt(II) complexes reported exhibit some interesting properties. All of them are luminescent both in fluid solution at room temperature and in a rigid matrix at 77 K from the lowest lying singlet $\pi-\pi^*$ excited state. The solvent dependence of the absorption and emission spectra indicates that a partial charge transfer is present in the (emitting) excited state in **1** and **3**.

The nature of the N-heterocyclic ligands and the spectroscopic and photophysical data suggest that such complexes could be useful as luminescent probes for biological applications.

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(31) *Topics in Applied Physics*; Schäser, F. P., Ed.; Springer-Verlag: Berlin and Heidelberg, 1973; Vol. 1.