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Polypyridine Ruthenium(II) Complexes Containing Mixed Ligands. Synthesis, Spectroscopic and Photophysical and Electrochemical Properties

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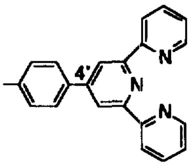
ABSTRACT

A series of polypyridine Ruthenium(II) complexes $Ru(II)(ttp)(L)X \times PF_6$ *were synthesized and characterized, where L are 2,2′-bipyridine(bpy), 4,4′-dimethyl-2,2′-bipyridine(dmpy), 1,10-phenanthroline(phen) and X are* Cl^-, NCS^-, CN^-; *ttp = 4′-p-tolyl-2,2′:6′,2″-terpyridine. Their redox, spectroscopic and photophysical properties have been studied. All complexes have intense* $MLCT(d_M \rightarrow \pi_L^*)$ *absorbance at approximately 500 nm and were found to be emitting with monoexponential decay of emission intensity at 298 K. The maximum wavelengths of absorbance and emission undergo a blue shift in the order of* Cl^-, NCS^-, CN^-. *All complexes have an one-electron-oxidative process corresponding to Ru(III)/Ru(II) with a potential of about 0.8 V, and their oxidation potential increased also according to* Cl^-, NCS^-, CN^-. *Two reversible or quasi-reversible one-electron-reductive processes based on ligands were also observed. © 1998 Elsevier Science Ltd*

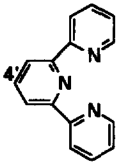
Keywords: Ruthenium(II), polypyridine complex, charge–transfer transition, cyclic voltammetry, time-resolved emission Spectra.

INTRODUCTION

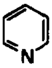
The investigation of Ru(II) polypyridine complexes has been attractive for more than two decades. These complexes as inorganic dyes possess highly versatile luminescent and photoredox properties, which have played and are still playing a very important role in the development of photochemistry, photophysics, photocatalysis, electrochemistry, photoelectrochemistry, and electron and energy transfer [1–4]. Ru(II) polypyridine complexes have an important feature in that their ground and excited state properties can be gradually changed by adequate choice and combination of ligands having different π-accepting and σ-donating abilities [5]. In the family of Ru(II) polypyridine complexes, there are two essential complexes Ru(II)(bpy)$_3$$^{2+}$ and Ru(II)(trpy)$_2$$^{2+}$, which have been investigated in great detail [1–4, 6, 7]. The former has a very long excited-state lifetime and strong room temperature emission [1, 8–10], and so emission and transient characterization are readily observable. It is of interest to probe the interaction between it and other substrates. Although the latter has a shorter excited-state lifetime and a much weaker luminescence in fluid solution at room temperature [11, 12], the geometry of Ru(II)(trpy)$_2$$^{2+}$ complexes, on the contrary, offers the possibility to design triads in which the two additional components are on opposite directions with respect to the photosensitizer. In addition, Ru(II)(trpy)$_2$$^{2+}$ complexes are achiral having two symmetry planes and C_2 axis, and the introduction of a single substituent at the 4′-position of each trpy ligand does not lead to isomeric mixtures. These triads are currently the object of extensive investigations [7, 13–16]. Compared with it, complexes containing mixed-ligand (trpy, bpy, etc.) and their derivatives have received less attention. However, this type of complexes are very effective photosensitizers in systems involving fast photoinduced electron transfer, such as in the dye-sensitized solar cell, etc. [17, 18], and for the study of the influences of ligands on the properties of complexes it is also a good system. In this paper we have synthesized a series of complexes containing mixed ligands and investigated their photophysical and electrochemical properties. The polypridine ligands often used are as follows:



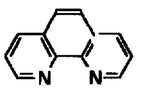
ttp



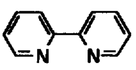
trpy



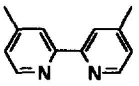
py



phen



bpy



dmpy

EXPERIMENTAL

Materials

Ruthenium(III)trichloride·3H$_2$O was obtained from Aldrich and potassium hexafluorophosphate from TOKYO ASEI.

Synthesis

4′*p*-Tolyl-2,2′:6′2,2″-terpyridine(ttp) [14], and Ru(ttp)Cl_3 [19] were prepared by literature methods.

[Ru(ttp)(bpy)Cl]·PF_6 (1): was prepared by a modification of the previous literature method [20]. Ru(ttp)Cl_3 (444 mg, 0.882 mmol), the ligand bpy (138 mg, 0.884 mmol) and LiCl (200 mg) were added to 80 ml of a 3:1(v/v) ethanol/water mixture. Triethylamine (0.9 ml) was added as a reductant, and the mixture was refluxed with stirring under N_2 for 4 h. This solution was concentrated to 20 ml by rotary evaporation and then added dropwise to 50 ml of saturated aqueous KPF_6. The resulting precipitate was separated by vacuum filtration, washed with chilled 3 M HCl, water and diethyl ether, and dried under vacuum. The crude product was then purified by alumina chromatography using 1:1(v/v) acetone/toluene as eluant. The desired product eluted first as a purple band; the eluant was rotary evaporated and the residue dissolved in a minimal amount of acetone and precipitated by addition to 100 ml ether. The precipitate was again isolated by vacuum filtration and washed with diethyl ether, giving 585 mg of a purple solid, yield 87%. Analysis calculated for $C_{32}H_{25}N_5ClPF_6Ru$: C, 50.5%; H, 3.31%; N, 9.20%. Found: C, 49.78%; H, 3.50%; N, 9.16%.

Ru(ttp)(bpy)NCS·PF_6 (2): A suspension of 210 mg (0.328 mmol) **1** and 110 mg (1.36 mmol) NaNCS in 40 ml of ethanol–water (1:1) mixture was refluxed under N_2 for 4 h. After cooling, 50 ml saturated aqueous solution of potassium hexafluorophosphate was added dropwise to the reaction mixture. The precipitate formed was filtered and washed successively with water (2×20 ml), toluene (2×20 ml) and ether (2×50 ml). The crude product was purified by neutral alumina chromatography twice, using 1:1 (v/v) acetone/toluene as eluent. After a small purple band of unreacted **1**, an orange band containing the desired product was eluted. This band was concentrated to induce precipitation, recrystallized from toluene/acetone (1:2,v/v) and gave orange crystals, yield: 77.7%. Analysis calculated for $C_{33}H_{25}N_6SPF_6Ru$: C, 50.58%; H, 3.22%; N, 10.72%. Found: C, 50.38%; H, 3.14%; N, 10.80%. IR (ν, cm 2096 (NCS).

[Ru(ttp)(bpy)CN]·PF_6 (3): 175 mg (0.230 mmol) [Ru(ttp)(bpy)Cl]·PF_6(**1**), 60 mg (0.92 mmol) KCN, 20 ml water; following the same procedure of reaction and purification as for Ru(ttp)(bpy)NCS·PF_6 (**2**), except that refluxing was carried out for 10 h, a light yellow solid **3** was obtained 95 mg, yield: 55%. Analysis calculated for $C_{33}H_{25}N_6PF_6Ru$: C, 52.73%; H, 3.35%; N, 11.18%. Found: C, 51.73%; H, 3.43%; N, 10.34%. IR (ν, cm^{-1}): 2079 (CN)

[Ru(ttp)(dmpy)Cl]·PF_6 (4): 460 mg (0.8671 mmol) Ru(ttp)CI_3, 160 mg (0.866 mmol) dmpy, 200 mg LiCl, 0.8 ml NEt_3; the same procedure of reaction and purification as for **1** gave **4** 500 mg, yield: 73%. Analysis calculated for $C_{34}H_{29}N_5ClPF_6Ru$: C, 51.75%; H, 3.70%; N, 8.87%. Found: C, 50.11%; H, 3.64%; N, 8.52%.

[Ru(ttp)(dmpy)SCN]·PF$_6$ (5): 200 mg (0.253 mmol) **4**, 20 ml water, 20 ml ethanol and 126 mg (1.55 mmol) NaNCS; the same procedure of reaction and purification as for **2** gave **5** 152 mg, yield: 74%. Analysis calculated for $C_{35}H_{29}N_6SPF_6Ru$: C, 51.79%; H, 3.60%; N, 10.35%. Found: C, 50.94%; H, 3.61%; N, 9.88%. IR (ν, cm^{-1}): 2096 (NCS).

[Ru(ttp)(dmpy)CN]·PF$_6$ (6): 198 mg (0.251 mmol) **4**, 70 mg KCN, 15 ml water, 15 ml ethanol; the same procedure of reaction and purification as for **3** gave **6** 152 mg, yield: 38%. Analysis calculated for $C_{35}H_{29}N_6PF_6Ru$: C, 53.92%; H, 3.75%; N, 10.78%. Found: C, 53.13%; H, 3 66%; N, 9.92%. IR (ν, cm^{-1}): 2075 (CN).

[Ru(ttp)(phen)Cl]·PF$_6$ (7): 457 mg (0.862 mmol) Ru(ttp)Cl$_3$, 171 mg Phen·H$_2$O, 200 mg LiCl, 0.5 ml Net$_3$; the same procedure of reaction and purification as for **1** gave **7** 533 mg, yield: 79%. Analysis calculated for $C_{34}H_{25}N_5ClPF_6Ru$: C, 52.02%; H, 3.21%; N, 8.92%. Found: C, 51.92%; H, 3.21%; N, 8.88%.

[Ru(ttp)(phen)SCN]·PF$_6$ (8): 170 mg (0.217 mmol) **7**, 150 mg NaNCS 25 ml water, 25 ml ethanol; the same procedure of reaction and purification as for **2** gave **8** 121 mg, yield: 69%. Analysis calculated for $C_{35}H_{25}N_6SPF_6Ru$: C, 52.05%; H, 3.12%; N, 10.40%. Found: C, 51.71%; H, 3.06%; N, 9.79%. IR (ν, cm^{-1}): 2093 (NCS).

[Ru(ttp)(phen)CN]·PF$_6$ (9): 279 mg (0.356 mmol) **7**, 90 mg KCN, 20 ml water, 20 ml ethanol the same procedure of reaction and purification as for **3** gave **9** 100 mg, yield: 36%. Analysis calculated for $C_{35}H_{25}N_6PF_6Ru$: C, 54.20%; H, 3.25%; N, 10.83%. Found: C, 53.98 %; H, 3.45 %, N, 10.33%. IR (ν, cm^{-1}): 2075 (CN).

Physical Measurements and Instrumentation

Spectroscopy

Absorption spectra were recorded using two matched 1 cm glass cells on a Shimadzu UV-1600A Recording Spectrophotometer. Samples were prepared gravimetrically as approximately 3×10^{-5} M of acetonitrile or methylene chloride solutions and studied at room temperature.

Infrared spectra were recorded on KBr pellets with a Perkin-Elmer 983G spectrometer. Emission spectra were recorded on a Perkin-Elmer LS-5 Fluorescencespectrometer and Perkin-Elmer 3600 Data Station. All measurements were made in a 1 cm fluorescence cell at right angles to the incident beam. Samples were prepared at about 3×10^{-5} M in argon purged acetonitrile or methylene chloride solutions. Emission spectra were collected using respective maxima absorption in the visible region as excitation wavelength and reported as uncorrected values. Excitation spectra were independent of the monitoring wavelength.

Emission lifetimes were measured by the nanosecond laser flash photolysis technique using a DCRNd:YAG laser (532 nm) as the excitation source and SMA(Spectrometrimetric Multichannel Analyzer, Princeton Intruments Inc. OSMA Detector Controller) as detector. The data were transferred to a 486 PC to make manipulation of logarithm or exponent for calculating lifetimes of the complexes.

Electrochemistry

Cyclic voltammograms were recorded on an M270C electrochemical system (EG&G Corp.). Measurements were made at a sweep rate of 100 m V/S. The adopted three-electrode system consisted of a Pt disc working electrode, a Pt wire counter electrode, and a saturated calomel reference electrode. The supporting electrolyte was 0.1 M *n*-tetrabutylammonium perchlorate in acetonitrile. Solutions of the samples (approximately 5×10^{-4} M) were prepared by dissolution in refined acetonitrile. The solutions were deoxygenated by bubbling with nitrogen for 15 min before each scan. The Pt working electrode was manually cleaned and polished prior each individual scan.

RESULTS AND DISCUSSION

Table 1 summarizes the electronic spectral data of these complexes. As with most of the other ruthenium(II) polypyridine complexes [1], the absorption spectra of complexes **1–9** are dominated by intense ligand-based ($\pi \rightarrow \pi*$) bands in the ultraviolet region, while charge-transfer(MLCT) bands are observed in the visible region of spectrum. The maximum absorption wavelengths of these complexes are blue shifted in the order of Cl–, NCS^- and CN^-, consistent with increase of the ligand fields. All these complexes exhibit solvent-dependent absorption spectra, with blue shifts of the absorption maxima and slightly increasing of their molar extinction coefficients on going from dichloromethane to acetonitrile. Table 2 summarizes the electrochemical data of the series of complexes. We observed a single metal-centered oxidation in the positive potential region and a successive ligand-based reduction in the negative potential region. These reductions correspond to the formation of radical anions as electrons are added to the $\pi*$ orbitals of the polypridine ligands. Compared with electrochemical actions of $Ru(II)(bpy)_3{}^{2+}$ [19, 21–23], and $Ru(II)(trpy)_2{}^{2+}$ [21] as well as Ru(II)(trpy)(bpy) L^{n+}($n=1$ or 2) [23], we can conclude that the electrochemical process is as follows:

TABLE 1
Absorption Spectra Data of Compounds **1–9**[a]

No.	λ_{max}^{abs} $(nm)^{a}$	$10^{-4}\varepsilon_{max}$ $(M^{-1}\ cm^{-1})^{b}$	λ_{max}^{abs} $(nm)^{c}$	$10^{-4}\varepsilon_{max}$ $(M^{-1}\ cm^{-1})^{c}$	λ_{max}^{em} $(nm)^{c}$	τ $(ns)^{c}$
1	510	1.32	514	1.30	742	13
	284	5.61	293	5.04		
	237	3.35	242	3.45		
2	499	1.42	500	1.31	710	10
	288	7.07	293	5.51		
	234	4.07	242	3.98		
3	494	1.41	499	1.39	660	9
	289	5.46	292	5.20		
	233	2.82	236	2.85		
4	516	1.43	518	1.32	750	22
	285	5.86	287	5.78		
	227	3.22	238	3.12		
5	506	1.34	516	1.24	715	20
	285	7.04	289	5.86		
	225	4.11	237	3.83		
6	496	1.67	503	1.45	670	12
	285	7.16	287	5.64		
			234	2.98		
7	510	1.65	519	1.56	740	14
	283	5.52	286	4.23		
	266	6.87	266	5.91		
	228	5.66	233	4.93		
8	503	1.48	514	1.43	714	14
	283	5.35	285	4.28		
	265	6.71	266	6.02		
	227	5.81	232	5.25		
9	496	1.33	499	1.23	660	—
	264	5.38	264	4.58		
	227	4.03	232	3.54		

[a] Absorption and emission acquired under room temperature.
[b] in CH_3CN.
[c] in CH_2Cl_2.

TABLE 2
Electrochemical Data of Compounds **1–9**[a]

No.	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
$E^{1/2}$	0.78	0.86	1.04	0.75	0.85	0.98	0.79	0.84	1.06
(ΔE,mV)	(71)	(124)	(98)	(67)	(43)	(67)	(85)	(165)	(61)
$E^{1/2}$	−1.37	−1.37	−1.34	−1.40	−1.39	−1.39	−1.39	−1.37	−1.36
(ΔE,mV)	(88)	(25)	(86)	(35)	(42)	(61)	(104)	(37)	(31)
$E^{1/2}$	−1.63	−1.67	−1.70	−1.64	−1.71	−1.74	−1.61	−1.65	−1.67
(ΔE,mV)	(64)	(67)	(73)	(80)	(61)	(129)	(80)	(40)	(53)

[a] All potentials via SCE, in CH_3CN and 0.1 M *n*-tetrabutylammonium perchlorate and room temperature, $E_{1/2} = (E_{ox} + E_{red})/2$ $\Delta E = E_{ox} - E_{red}$.

$$[\mathrm{Ru^{III}(ttp)(L)X}]^{2+} \underset{-e}{\overset{+e}{\rightleftharpoons}} [\mathrm{Ru^{II}(ttp)(L)X}] \underset{-e}{\overset{+e}{\rightleftharpoons}}$$

$$[\mathrm{Ru^{II}(ttp^{\bullet -})(L)X}]^{0} \underset{-e}{\overset{+e}{\rightleftharpoons}} [\mathrm{Ru^{II}(ttp^{\bullet -})(L^{\bullet -})X}]^{1-}$$

With respect to the oxidative potentials of $\mathrm{Ru(II)(bpy)_3}^{2+}$, $\mathrm{Ru(II)(trpy)_2}^{2+}$ and $\mathrm{Ru(II)(trpy)(bpy)L}^{2+}$ ($\mathrm{L} = \mathrm{py}$ or its derivatives), the oxidative potentials of compounds **1–9** are obviously less positive. The monodentate ligands of $\mathrm{Cl^-}$, $\mathrm{NCS^-}$ and $\mathrm{CN^-}$ are stronger σ-electron donors than the ligands of trpy, bpy and py, which gave rise to a increasing charge localized on Ru(II) and so the complexes **1–9** easily lose an electron and show lower oxidative potentials. Stepwise increasing oxidative potentials of **1–9** with $\mathrm{Cl^-}$, $\mathrm{NCS^-}$, $\mathrm{CN^-}$ were observed. The ligand fields of complexes **1–9** become stronger and their crystal field stabilization energy increases, and the orbital energy of $\mathrm{Ru(t_{ag})}$ decreases in the order of $\mathrm{Cl^-}$, $\mathrm{NCS^-}$, $\mathrm{CN^-}$, which make loss of an electron of the orbital $\mathrm{Ru(t_{2g})}$ more difficult, and the oxidative potentials increase in the same order.

Similarly, because of the stronger σ-donating abilities of the ligands of $\mathrm{Cl^-}$, $\mathrm{NCS^-}$, $\mathrm{CN^-}$ compared to the ligands of ttp, bpy, py, etc., the ligands of ttp, bpy, dmpy and phen in the complexes of **1–9** should experience more electronic charge coming from the orbital $\mathrm{Ru(t_{2g})}$. This means that the ligands in the compounds **1–9** accept an electron with more difficulty than the corresponding ligands in the complexes of $\mathrm{Ru(ttp)_2}^{2+}$, $\mathrm{Ru(trpy)(bpy)(py)}^{2+}$ and $\mathrm{Ru(bpy)_3}^{2+}$, and their reduction potentials are hence more negative ($E_{\mathrm{trpy/trpy-}} \approx -1.26\,\mathrm{V}$ in $\mathrm{Ru(trpy)_2}^{2+}$ [1]; $E_{\mathrm{trpy/trpy-}} \approx -1.26\,\mathrm{V}$, $E_{\mathrm{bpy/bpy-}} \approx -1.55\,\mathrm{V}$ in $\mathrm{Ru(trpy)(bpy)(py)}^{2+}$ [23], and $E_{\mathrm{ttp/ttp-}} \approx -1.24\,\mathrm{V}$ in $\mathrm{Ru(ttp)_2}^{2+}$ [7]). We also observed that the reductive potential $E_{\mathrm{ttp/ttp-}}$ varied irregularly between -1.34 and $-1.40\,\mathrm{V}$; however, the reductive potentials of the bidentate ligands(bpy, dmpy, phen) changed regularly and that is why the reductive potential of the same bidentate ligand shifts to more negative in the order of $\mathrm{Cl^-}$, $\mathrm{NCS^-}$, $\mathrm{CN^-}$. From the crystal structure of $\mathrm{Ru(trpy)(bpy)(py){\cdot}2PF_6}$ [23], we know that the monodentate ligands are *trans* to one ring of the bidentate ligands while all three rings of the terpyridine are in *cis* orientation with respect to monodentate ligand. Thus, bidentate ligands should feel any electronic variation due to the changing monodentate ligands to a greater extent than the tridentate ligand. As the bidentate ligands (bpy, dmpy, phen) were influenced more intensively by monodentate ligand coordination, their reductive potential show some regularity.

Emission spectra and emission lifetimes: all of the complexes show room temperature emission and the emission maxim undergo a red shift in the order of $\mathrm{CN^-}$, $\mathrm{NCS^-}$, $\mathrm{Cl^-}$, consistent with absorption. As the weak emission, a time-correlated single photo counting method can not be used to determine the lifetimes of our complexes, the laser flash photolysis technique was adopted to obtain time-resolved emission decay curves of complexes **1–8** (Fig. 1) and the logarithm of the emission intensity with decay time is good linear relationship (Fig. 2).

By the slopes of these lines, the lifetimes of the complexes **1–8** were calculated, which are in the 9–22 ns range, longer than that of $\mathrm{Ru(ttp)_2}^{2+}$ and $\mathrm{Ru(trpy)_2}^{2+}$, and emission intensity also become intense (usually, room

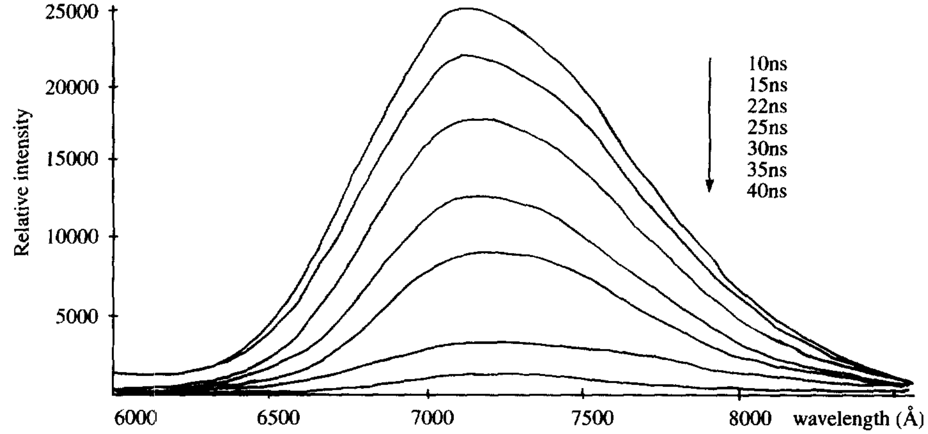


Fig. 1. Transient emission spectrum of **2** (in CH_2Cl_2, room temperature).

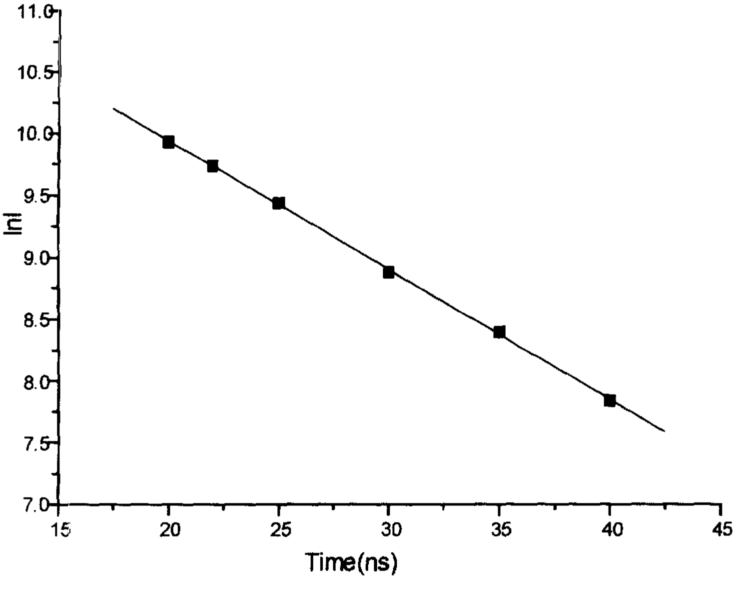


Fig. 2. Relationship of logarithm of the emission intensity of complex **2** with decay time.

temperature emission of $Ru(ttp)_2{}^{2+}$ or $Ru(trpy)_2{}^{2+}$ is not observed). But, both lifetime and intensity are far smaller than that of $Ru(bpy)_3{}^{2+}$.

CONCLUSION

A series of complexes of $Ru(II)(ttp)(L)X^+ \times PF_6(X = Cl^-, NCS^-, CN^-)$ were synthesized and their photophysical and electrochemical properties were also studied. Their photophysical properties are between those of $Ru(bpy)_3{}^{2+}$ and $Ru(ttp)_2{}^{2+}$. These complexes are better electron donors compared with their parent complexes of $Ru(bpy)_3{}^{2+}$ and $Ru(ttp)_2{}^{2+}$. The monodentate ligands (Cl^-, NCS^-, CN^-) have a more obvious influence on the properties of the complexes than the bidentate, possibly because the differences in the properties of bpy, dmpy and phen are very small.

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