

 Polyhedron Vol. 17, No. 18, pp. 3071–3082, 1998

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 0277–5387/98
 \$19.00+0.00

PII: S0277-5387(98)00074-6

Synthesis, spectroscopic, photophysical and electrochemical properties of cyano-bridged copper(I)-ruthenium(II) complexes

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(Received 20 August 1997; accepted 12 February 1998)

Abstract—Complexes of the formula [(N–N)Cu(AsPh₃)CN] (N–N=2,2'–bipyridine, 1,10–phenanthroline) have been synthesized. Ru(bpy)₂Cl₂.2H₂O and [(η^5 –cp)Ru(PPh₃)₂Cl] react with [(N–N)Cu(AsPh₃)CN] to give cyano-bridged compounds. IR spectral studies in the low frequency region (700–50 cm⁻¹) and 4000–400 cm⁻¹ region reveal cyano bridging in the complexes. Luminescence measurements suggest oxidation of metal centres (Cu^I–Cu^{II} and Ru^{II}–Ru^{III}) on excitation at a charge transfer band. This has been substantiated with electrochemical studies of complexes which exhibit quasi-reversible reductions viz. Ru^{III}/Ru^{II} and Cu^{II}/Cu^I. The deposition of metallic copper is also observed at a potential of –1.55 V. Based on these data, a mechanism for photo-redox reaction of complexes has been presented. The properties of these bimetallic complexes are compared with those of parent complexes. © 1998 Elsevier Science Ltd. All rights reserved. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: synthesis; binuclear complexes; FTIR, quasi-reversible; luminescence; electron-transfer.

Solar energy is the largest energy source available to mankind but its utilization in comparison to its availability is negligible. The design of suitable chromophores to be used as sensitizers in this process is one of the aims of co-ordination chemists [1]. Mononuclear and binuclear Ru^{II} polypyridine complexes show remarkable sensitizing properties [2, 3]. Such systems are also involved in electron-transfer and energy transfer processes [4]. In recent years much work has been done on cyanobridged homo and hetero/polynuclear complexes [5] to explore the various photophysical properties, including sensitization.

There are some reports on heteronuclear cyanide [6] bridged complexes containing Ru^{II} and other metal centres. We have been interested in the properties of cyano bridged bimetallic complexes and our earlier studies on these systems have highlighted some of the interesting properties [7]. In continuation, in this paper we wish to report the electrochemical, photophysical and spectral studies on a variety of cyanobridged $Cu^{I}-Ru^{II}$ complexes. The stimulation for photophysical studies of bridged systems is based on

the fact that Cu¹ complexes independently exhibit luminescence [8].

1. EXPERIMENTAL

¹H NMR spectroscopy was carried out on a Bruker WP-80 and a Bruker DRX300 spectrometer in the range 0–10 ppm (δ) using TMS as an internal calibrant. A COSY two-dimensional experiment was carried out on the Bruker DRX 300. ¹³C NMR spectroscopy was carried out on a Bruker WP-80 and a Bruker DRX300 spectrometer. IR spectra were recorded on a Shimadzu IR 420 Spectrophotometer as KBr pellets in the 4000–400 cm⁻¹ range, FTIR spectra on a Perkin-Elmer FTIR 1700X Spectrophotometer in Nujol mull with polyethylene plates in the range 700-50 cm⁻¹. UV-Vis spectra were carried out on a Shimadzu double beam UV-160 spectrophotometer in acetonitrile. Melting points were obtained on a Fisher-John melting point apparatus and are uncorrected. Conductivity measurements were carried out in acetonitrile on a Toshniwal Conductivity Bridge. Microanalyses were performed at the RSIC, CDRI, Lucknow, India.

Emission spectra were recorded on a Perkin-Elmer

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Luminescence Spectrophotometer LS50B. Correction of the luminescence intensity profile was performed by fluorescence data manager software. Luminescence quantum yields ϕ_s were evaluated by comparing areas under the corrected luminescence spectra on an energy scale and by using the following equation:

$$\frac{\phi_s}{\phi_r} = \frac{F_s \cdot A_r}{F_r \cdot A_s}$$

where the F_s and F_r are the integrated fluorescence intensities of the sample and $[Ru(bpy)_3]^{2+}$. A_s and A_r are the absorbance of the sample and $[Ru(bpy)_3]^{2+}$ at excitation of same wavelength. ϕ_r for $[Ru(bpy)_3]^{2+}$ is taken as 0.028.

For the lifetime measurements a coherent synchronously pumped cavity dumped dye laser (702-1) pumped by a coherent CW mode-locked Nd:YAG laser (Antares 76s) was used. The fundamental laser light at 600 nm was frequency doubled to produce exciting light at 300 nm. The emissions were detected at a magic angle of 54.7° polarisation using a Hamamatsu MCP photomultiplier tube (2809U). The response time of the setup is 50–60 ps.

The FAB mass spectra were recorded on a JEOL SX 102/DA-6000 system using Xenon (6 kV, 100 mA) as the FAB gas and *m*-nitrobenzyl alcohol as a matrix.

Cyclic voltammograms were recorded on a Bio-Analytical System-27 electrochemical analyser, utilizing a three electrode configuration, consisting of a glassy carbon working electrode, Pt wire auxiliary electrode and Ag/AgCl reference electrode. An omnigraphic model 100X-Y recorder was used to record the current-voltage output.

RuCl₃.xH₂O was obtained from Loba Chemie and triphenylarsine, 2,2'-bipyridine and 1, 10-phenanthroline from E-Merck and used as received; Acetonitrile (Qualigens) used in electrochemical and spectroscopic studies was dried over molecular sieves. All other chemicals used were either AnalaR grade or chemically pure. Manipulations were invariably performed under oxygen free dry nitrogen atmosphere using standard schelnk line and other techniques [9]. The solvents were dried using standard procedures before use.

Ru(bpy)₂Cl₂.2H₂O [10] and $[(\eta^5 - cp)Ru(PPh_3)_2Cl]$ [11] were prepared according to methods in literature. CuCN, Cu(AsPh_3)₂CN and their substituted analogues were prepared by modifying the literature procedures [7, 12].

1.1. Syntheses

1.1.1. Cyanobis–(triphenylarsine)copper(I); [Cu(A-sPh_3)₂CN] [1] To a suspension of CuCN (0.895 g, 0.01 mole) in chloroform (50 cm³) was added a solution of triphenylarsine (12.258 g, 0.04 mole) in chloroform (70 cm³), and the reaction mixture was stirred constantly for an hour. During the course of the reaction the desired complex was precipitated. The volume of

the reaction mixture was reduced in a rotatory evaporator. While removing the solvent, a white precipitate dissolved and a thick viscous liquid appeared. It was cooled and then treated with benzene (40 cm^3) which resulted in superfine white crystals. These were then filtered and washed with dry ether and then dried *in vaccuo*.

1.1.2. Cyanobipyridine(triphenylarsine)copper(I); Cu(AsPh₃)(bpy)CN [2] To a suspension of Cu(AsPh₃)₂(CN) (0.701 g, 1 mmol) in benzene (30 cm³) was added a solution of bipyridine (0.156 g, 1 mmol) in benzene (30 cm³) with constant stirring. The resulting yellow solution was refluxed for 2–3 hours. The clear solution thus obtained was cooled, the volume was reduced to half and excess petroleum ether (60–80°C) was added, which resulted in the precipitation of a pale-yellow compound. It was filtered, washed several times with petroleum ether and dried *in vaccuo*. It was recrystalized from a CHCl₃–xylene mixture (1:1).

1.1.3. Cyano1,10-phenanthroline(triphenylarsine) copper[I]: [Cu(AsPh₃)(phen)CN] [3] To a suspension of Cu(AsPh₃)₂CN] (0.701 g, 1 mmol) in benzene (30 cm³) was added a solution of 1,10. phenanthroline (0.198 g, 1 mmol) in benzene (30 cm³) with constant stirring. Immediately an orange-red precipitate appeared, the resulting mixture was refluxed for an hour. After cooling, excess petroleum ether (60–80°C, 100 cm³) was added to ensure complete precipitation of the complex. The complex was centrifuged and washed several times with petroleum ether and dried *in vaccuo*. It was recrystalized from a CHCl₃-xylene mixture (1:1).

1.1.4. Bis-(triphenylarsine)copper(I)(μ -cyano)chlorobis-(2,2'-bipyridine)ruthenium(II)hexafluorophosphate; [((AsPh₃)₂Cu-CN-Ru(bpy)₂Cl] PF₆.[4] A mixture of [Cu(AsPh₃)₂CN] (0.701 g, 1 mmol) and Ru(bpy)₂Cl₂.2H₂O (0.512 g, 1 mmol) was suspended in ethanol (50 cm³) and the suspension was refluxed for an hour. The solution was cooled and filtered. A highly concentrated solution of NH₄PF₆ in water (0.0064 g in 1 cm³) was added, which caused the immediate precipitation of a complex. The precipitate was washed thoroughly with water and then with ether, and dried over P₄O₁₀ for several hours. It was recrystalized from a CHCl₃-CH₃CN mixture (1:1).

1.1.5. Bis–(triphenylarsine)copper(I)(μ –cyano)cyclopentadienylbis–(triphenylphosphine)rutherium (II)hexafluorophosphate; [(AsPh₃)₂Cu–CN–Ru(η^{5} – cp) (PPh₃)₂]PF₆ [5] [Cu(AsPh₃)₂CN] (0.701 g, 1 mmol) and (η^{5} –cp)Ru(PPh₃)₂Cl] (0.725 g, 1 mmol) were taken in methanol (50 cm³) and the mixture was stirred vigorously. NH₄PF₆ (0.174 g, 1.2 mmol) was added to this solution and refluxed for an hour, which upon cooling gave a pale yellow precipitate. The solvent was evaporated to dryness *in vaccuo* and the residue was extracted with a small amount of dichloromethane and filtered. On addition of excess petroleum ether (60–80°C), a complex precipitated, which was centrifuged and washed several times with petroleum ether and dried in vaccuo. It was recrystalized from CHCl₃.

(1,10–Phenanthroline)(triphenylarsine) 1.1.6. $copper(I)(\mu$ -cyano)chlorobis-(2,2'-bipyridine)ruthenium(II)hexafluorophosphate; [(phen)(AsPh₃)Cu- $CN-Ru(bpy)_2Cl]PF_6$ [6] [Cu(AsPh₃)(phen)CN] (0.179 g, 0.2 mmol) and Ru(bpy)₂Cl₂.2H₂O (0.104 g, 0.2 mmol) were dissolved in a 1:1 mixture of water and ethanol (50 cm³), and the solution was refluxed for 5 hours. The resulting solution was cooled and filtered. To this filtrate was added a concentrated aqueous solution of NH_4PF_6 (0.0064 g/cm³). A precipitate of maroon colour immediately appeared, which was centrifuged and washed several times with ether and dried over P_4O_{10} for several hours in vaccuo. It was recrystalized from a CHCl₃-CH₃CN mixture (1:1).

1.1.7. $(2,2'-Bipyridine)(triphenylarsine)copper(I)(\mu$ cyano)chlorobis-(2,2'-bipyridine) ruthenium(II) hexafluorophosphate; [(bpy)(AsPh₃)Cu-CN-Ru(bpy)₂ Cl]PF₆.[7] The same as in Section 1.1.6, except [Cu(AsPh₃)(bpy)CN] was used in place of [Cu(As Ph₃)(phen)CN].

2. RESULTS AND DISCUSSION

The analytical data for the complexes are given in Table 1, which are consistent with the stoichiometries proposed. The conductivity data of the complexes [1], [2], and [3] show a non-electrolytic nature, whereas other cation complexes are 1:1 electrolytes [13]. All the complexes are diamagnetic at room temperature.

FAB mass spectral data are assigned in Table 2. The molecular ion peak usually is of a low intensity. All the complexes show a M–PF₆ peak. Other isotopic peaks are also observed and appear as bands. Some of these are summarized in Table 2. The variation in the m/z values is mainly due to presence of the heavier atom isotopes of ruthenium (96-104), Cu(63,65) and Cl(35,37). In Complex [5], M-PF₆ shows large variation. This may be due to the presence of seventy-eight carbon atoms. The effect diminishes as the number of carbons decreases in other complexes. The peak at m/z = 123.5 [5] indicates dissociation of AsPh₃ and facile rearrangement of counter anion at copper centre to produce neutral complex. This is also observed in complex [7].

2.1. IR spectra

The v_{CN} stretching frequency data of the complexes [1]–[7] are given in Table 3. For complex [1], v_{CN} at 2130 cm^{-1} (lit. value [14] 2125 cm^{-1}) indicates that the CN group is terminal. Lowering of v_{CN} in complexes [2] and [3] may be due to an increase in coordination number [7, 15]. Further lowering of v_{CN} stretching on bridging in complexes [4]–[7] is due to enhanced π back donation from ruthenium and copper [7].

IR spectral data in the low frequency region of

Complex	Colour		Analysis Found (Calc) (%)		mp $a \; heta/^{\circ} \mathrm{C}$	$\operatorname{Yieldb}(\%)$	$\Omega - 1 \text{ cm}^2 \text{ mol}^{-1}$ Conductivity
		C	Н	Z			
Cu(AsPh ₃) ₂ CN] [1]	White	63.21 (63.30)	4.22 (4.30)	1.97 (1.99)	182	87.7	
Cu(AsPh ₃)(bpy)CN] [2]	Dark yellow	63.0 (63.10)	4.10 (4.17)	7.60 (7.61)	200 (d)	74.0	
Cu(AsPh ₃)(phen)CN] [3]	Dark Orange	64.40 (64.46)	3.80(3.99)	7.25 (7.29)	220 (d)	87.7	
$AsPh_3)_2Cu(\mu-CN)Ru(bpy)_2Cl]PF_6[4]$	Orange red	52.62 (52.82)	3.51 (3.50)	5.40(5.40)	177 (d)	81.2	126.8
$(AsPh_3)_2Cu(\mu-CN)Ru(\eta^5-cp) (PPh_3)_2]PF_6$ [5]	Light yellow	60.70 (60.7)	4.20 (4.21)	1.10(0.9)	136 (d)	63.3	154.4
$(phen)[(AsPh_3)_2Cu(\mu-CN)Ru(bpy)_2Cl]PF_6[6]$	Maroon	52.20 (52.30)	3.30(3.30)	8.30 (8.38)	184 (d)	72.2	158.0
$(bpy)[(AsPh_3)_2Cu(\mu-CN)Ru(bpy)_2Cl]PF_6$ [7]	Orange red	51.2 (51.35)	3.0 (3.05)	8.50 (8.55)	198 (d)	60.7	138.0
a d denotes decomposition temperature.							

Fable 1. Analytical and Physical data of the Complexes

b based on Copper compounds 1, 2, and 3 and on Ruthenium for the other compounds.

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Complex	m/z, found (Calc.) {r.a} a	Assignments
[5]	1541 (1541){10}	[⁶⁵ Cu–CN– ¹⁰⁴ Ru]PF ₆
	1536 (1536) {3}	$[^{63}Cu-CN-^{101}Ru]PF_{6}$
	1409 (1396){8}	$[^{65}Cu-CN-^{104}Ru]^+$
	1405 (1391) {3}	$[^{63}Cu-CN-^{101}Ru]^+$
	1235 (1235){12}	$[(PF_6)^{65}Cu-CN-^{104}Ru]$
[6]	1175 (1175){6}	[⁶⁵ Cu–CN– ¹⁰⁴ Ru(³⁷ Cl)]PF
	1170 (1170){4}	[⁶³ Cu–CN– ¹⁰¹ Ru(³⁷ Cl)]PF
	1168 (1168){5}	[⁶³ Cu–CN– ¹⁰¹ Ru(³⁵ Cl)]PF
	1030 (1030) {7}	[⁶⁵ Cu–CN– ¹⁰⁴ Ru(³⁷ Cl)] ⁺
	1025 (1025){12}	$[^{63}Cu-CN-^{101}Ru(^{37}Cl)]^+$
	1023 (1023){10}	[63Cu-CN-101Ru(35Cl)]+
[7]	1151 (1151){3}	[65Cu-CN-104Ru(37Cl)]PF
	1146 (1146){4}	[⁶³ Cu–CN– ¹⁰¹ Ru(³⁷ Cl)]PF
	1144 (1144){4}	[63Cu-CN-101Ru(35Cl)]PF
	1006 (1006){19}	$[^{65}Cu-CN-^{104}Ru(^{37}Cl)]^+$
	1001 (1001){17}	[⁶³ Cu–CN– ¹⁰¹ Ru(³⁷ Cl)] ⁺
	999 (999) {21}	$[^{63}Cu-CN-^{101}Ru(^{35}Cl)]^+$
	838 (838){19}	$[PF_6]^{63}Cu-CN-^{101}Ru(^{35}Cl)$

Table 2. FAB Mass Spectra

a r.a. stands for relative abundance.

Table 3. IR, FTIR and NMR Spectral data

Complex	IR Spectra (cm-1)					NMR Spectra (δ ppm)		
	v _{cn} a	$\upsilon_{Cu-AS} \ ^{b}$	$\delta_{\rm Cu-CN}{}^{\rm b}$	$v_{\text{Cu-C}} b$	υ _{Ru-N} b	¹ H	¹³ C	
[1]	2130	282	314	364	—	7.40 <i>d</i> (S, 30H)	128–135 <i>c</i> (phenyl) 137.0 (CN)	
[2]	2115				_	_		
[3]	2110	_				—	_	
[4]	2080	295 (m)	319 (sh)	352 (sh)	334 (s)	—	123.7–157.3 <i>c</i> (bpy, phenyl)	
[5]	2060	288 (m)	300 (w)	347 (sh)	_	7.09–7.37 <i>d</i> (m, 60H) 4.43 ^d (s, cp)	128.5–137.5 ^d 85.9 (cp)	
[6]	2090	292(s)	309 (w)	363 (m)	331 (m)	_	_	
[7]	2100	290 (w)	311 (vw)	362 (vw)	331 (m)	—	—	

a in KBr pellets

b in polyethylene plates

c recorded at 300 MHz in DMSO-d₆ and

d recorded at 80 MHz in CDCl₃.

The ¹³C NMR of bridging cyano group was not observed.

m stands for medium, s sharp, sh shoulder, w weak, vw very weak.

complexes [1]–[7] are given in Table 3. A representative FTIR spectra of complexes [1], [4] and [5] are shown in Fig. 1. The characteristics v_{Ru-N} , v_{Cu-C} , v_{Cu-As} and δ_{Cu-CN} have been assigned according to literature data [16–22]. We find that similar spectral patterns also appear for new cyano bridged complexes. It is seen that some of the ligand vibrations which do not appear in the free ligand are activated

by complex formation [20]. The splitting of some asymmetric bands are ascribed to lattice effect [22].

2.2. NMR spectra

The ¹H NMR and ¹³C NMR spectral data are given in Table 3. The proton NMR of complex [**5**] having



Fig. 1. Low Frequency IR spectra between 700 and 50 cm⁻¹ of complexes [1], [4] and [5].

 η^5 -cp group shows a sharp singlet signal at 4.43 ppm (δ). The cp peak of a complex shifts slightly to higher δ in comparison to the parent complex $[(\eta^5 - cp)Ru(PPh_3)_2Cl]$ [23]. The shift in δ value of cp protons in this complex suggests that the complex must be cationic in nature [24]. The proton signals of the phenyl groups appear in the region 7.0–8.0 as a broad multiplet [7].

Compound [4], [Fig. 2(a)], shows a complex pattern of resonance for which reliable assignment is not possible. To solve this problem spectra are assigned on the basis of a COSY two-dimensional experiment. Compound [4] is warmed to 120°C for a few minutes and then cooled before the spectrum was recorded. Two doublets are exhibited in the low-field area of the NMR spectrum and are found to be similar to the spectra reported in the literature [25, 26], whereas a multiplet is also observed in the region 7.0–8.8 ppm(δ) which cannot be assigned specifically [Fig. 2(b)]. These doublets are assigned as $H^{6'}$ of bpy (A) and bpy (B) at 10.02 and 9.52 ppm (δ), respectively [Fig. 2(b)]. Appearance of these signals is due to different spatial interaction of the chloride ligand [26]. On further heating for one hour the spectra was recorded by suppressing phenyl protons. The spectrum indicated that the above multiplet has also fragmented into sharp signals [27] [Fig. 2(c)].

The ¹³C NMR spectra of complex [1] exhibit NMR signals in the expected region of the phenyl group [28]. But in the case of complex [5], these signals were complicated and could not be specifically assigned. Nevertheless it can be said that the peak observed at 85.9 ppm (δ) for the cp group bound to ruthenium falls in the expected region [29].

2.3. UV-Vis spectra

Ground state absorption properties are summarised in Table 4, and the spectra of mononuclear and hetrobinuclear complexes are illustrated in Fig. 3. All the spectra were recorded in acetonitrile solution at room temperature. In cyanobridged complexes [4], [6] and [7] five bands are observed. These bands are characteristic bands of the Ru(bpy)²⁺₂ chromophores [10, 30, 31]. Bands at 245, 246 and 244 nm in these complexes [4], [6] and [7] respectively are assigned as $\pi \rightarrow \pi^*$ (bpy) intraligand transition and $\pi \rightarrow \pi^*$ (phenyl) AsPh₃ transitions.

Small blue shifts are observed in comparison to Ru(bpy)₂Cl₂.2H₂O. A similar pattern of shifting has been observed for bands in the 280-290 nm range, which are characteristic of ligand-centred (LC) $\pi \rightarrow$ π^* (bpy) transitions. Assignment of bands at 346 nm $[d\pi(Ru) \rightarrow \pi^* (bpy)]$ and at 480 nm $[d\pi(Ru) \rightarrow \pi^* (bpy)]$ in complex [4] as metal-to-ligand charge transfer (MLCT) is based on literature reports [10, 30, 31]. Comparing these bands to corresponding values of $Ru(bpy)_2Cl_2.2H_2O$ ($\lambda_{max} = 382 \text{ nm}$ and 551 nm), we infer that when the CN- ligand is attached to the $Ru(bpy)^{2+}{}_{2}$ moiety, there is an appreciable decrease in Ru→bpy π -backbonding. In this complex due to strong backbonding from Ru(II) to the cyano group, blue shift is observed, which is possible only when dorbitals are increasingly stabilised. These bands predict the possibility of CN-Ru interaction. High energy bands, λ_{max} at 210 nm in [4], 213 nm in [6] and 209 nm in [7], are characteristics of $[d\pi(Ru) \rightarrow \pi^*(CN)]$ MLCT transitions [32]. Thus, a possible explanation for the spectroscopic behaviour could be based on the fact that there are two types of Ru→Ligand MLCT transitions, one involving a terminal bpy ligand and the other involving a bridging CN- ligand. This has been supported by electrochemical results.

The absorption characteristics of [5] are similar to those of the well known analogue [7], $[(PPh_3)_2Cu - CN - Ru(\eta^5 - cp)(PPh_3)_2]PF_6$. The MLCT transitions at 357.0 nm of complex $[(\eta^5 - cp)Ru(PPh_3)_2Cl]$ is blue shifted which indicates the



Fig. 2. a) The structure of $[(AsPh_3)_2Cu-CN-Ru(bpy)_2Cl]^+$ and the numbering of protons of bpy ligands A and B in different environment.b) 300 MHz COSY ²D-NMR spectrum of [4] recorded in DMSO-d⁶. Assignment of the multiplet in the range 7.5-8.8 could not be made because of the complexity of the multiplet.c) 300 MHz COSY ²D-NMR spectrum of [4] recorded in DMSO-d⁶. Assignment of all protons are given as follows: bpy (A); **6**' (10.02), **5**' (7.85), **4**' (8.23), **3**' (8.75), **3** (8.68), **4** (8.06), **5** (7.14), **6** (7.80), and bpy (B); **6**' (9.52), **5**' (7.98), **4**' (8.40), **3**' (8.83), **3** (8.68), **4**(8.06), **5** (7.42), **6** (7.95) {ppm(δ }.

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increasing stabilisation of ruthenium d-orbitals by backbonding from the ruthenium to the cyanide group. On bridge formation the MLCT transition at 246 nm in the complex becomes broad and appears as a shoulder. Such shifting is also observed in complexes [4]-[7], and is in good agreement with the shifting of $v_{\rm CN}$ to low energy IR spectra. Complexes [2] and [3] give absorption bands at 357.5 nm and 363 nm respectively which are assigned as MLCT transitions and other bands are intraligand transitions [33]. The band at 269.0 nm of complex [3] appears as a shoulder on the band at 285.0 nm of complex [6]. Similarly the band at 284.0 nm of complex [2] appears as a shoulder on the band at 289.0 nm of complex [7]. No shoulder is observed in the electronic spectra of complex [4] because the band at 246.0 nm of [1] gets buried at the same λ_{max} .

2.4. Electrochemical properties

The electrochemical behaviour of a heterobinuclear cyano bridged system has been discussed previously [6], where ruthenium is one of the metal centres. Fig. 4 shows the voltammogram (vs Ag–AgCl in acetonitrile) of [6], at a scan rate of 100 mV/sec. $E_{1/2}$ values were obtained from the formula $E_{1/2} = \frac{E_{\text{pa}} + E_{\text{pc}}}{2}$. All of the waves with δE_{p} which are close to the values of δE_{p} for [Ru(bpy)₃]²⁺ ($E_{1/2} = 1.40$ V Vs Ag/AgCl [34], $\delta E_{\text{p}} = 90-120$ mV at a scan rate of 100 mV/sec) are reversible. All the other waves can be regarded as quasi-reversible. This compound shows two quasi-reversible responses at 0.76 V ($E_{\text{pa}} = 0.78$ V and $E_{\text{pc}} = 0.73$ V) and 1.27 V ($E_{\text{pa}} = 1.30$ V and $E_{\text{pc}} = 1.24$ V) which are attributed to the processes

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Complex	UV-Vis Bandsa				
	$\frac{\lambda_{\max} \text{ (nm)}}{\{10^{-4} \epsilon \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}\}}$	Assignment			
[1]	246 (4.59)	СТ			
	218 (7.18)				
[2]	357.5 (sh) (1.5)	CT			
	284 (2.52)				
	223 (6.52)				
[3]	363.0 (<i>sh</i>) (1.3)	CT			
	269 (5.69)				
	226 (8.38)				
[4]	482 (1.27)	$d\pi(Ru) \rightarrow \pi^*$ (bpy) CT			
	346 (1.37)	$d\pi(Ru) \rightarrow \pi^*$ (bpy) CT			
	288 (5.79)	$\pi \rightarrow \pi^*(\text{bpy}) \text{ CT}$			
	245 (2.18)	$\pi \rightarrow \pi^*(bpy)$ IL			
	210 (3.55)				
[5]	266 (sh) (4.86)	CT			
	223 (13.37)				
[6]	480 (1.32)	$d\pi(Ru) \rightarrow \pi^*$ (bpy) CT			
	346 (1.47)	$d\pi(Ru) \rightarrow \pi^*$ (bpy) CT			
	285 (6.33)	$\pi \rightarrow \pi^*(bpy)$ IL			
	246 (2.52)	$\pi \rightarrow \pi^*(bpy)$ IL			
[7]	484 (0.98)	$d\pi(Ru) \rightarrow \pi^*$ (bpy) CT			
	346 (1.05)	$d\pi(Ru) \rightarrow \pi^*$ (bpy) CT			
	289 (4.70)	$\pi \rightarrow \pi^*(\text{bpy}) \text{ IL}$			
	244 (1.33)	$\pi \rightarrow \pi^*(bpy)$ IL			
	209 (1.34)				

Table 4. Absorption spectral data

a recorded in acetonitrile solution, sh denotes shoulder.



Fig. 3. The electronic (UV-Vis) spectra of complexes [4], [6], [7] and $[Ru(bpy)_2Cl_2]2H_2O$.

 $Cu^{I} \rightarrow Cu^{II}$ and $Ru^{II} \rightarrow Ru^{III}$ corresponding to a phenanthroline bound copper metal centre and a bipyridine bound ruthenium metal centre respectively. The latter is consistent with literature values [32, 33]. The

 $E_{1/2}$ value for ligand reduction appears at -1.18 V which can be assigned to a copper bound phenanthroline reduction. Thus, the given ligand system can also stabilize the dinuclear cyano bridged com-



Fig. 4. Cyclic Voltammogram of complex [6] (vs Ag–AgCl in acetonitrile; 0.1 mol/dm³ tetrabutylammonium hexafluorophosphate and scan rate 100 mV/sec; 25°C).

plexes in a higher oxidation state i.e., the Cu^{II}–CN– Ru^{III} form. Such a mechanism depends on the ability of the cyanide ligand to act as a conducting bridge and, moreover, it involves intramolecular electron transfer.

There is one irreversible reductive wave with $E_{\rm red} = -1.55 \,\mathrm{V}$ attributable to the process $\mathrm{Cu}^{\mathrm{I}} \rightarrow \mathrm{Cu}^{0}$ [35]. This shows the deposition of copper metal at the electrode. It is believed that the $E_{1/2}$ value for bipyridine ligand reduction has merged with $\mathrm{Cu}^{\mathrm{I}}/\mathrm{Cu}^{0}$ reduction value. The other $E_{1/2}$ value does not occur due to the narrow window range. A comparison of electrochemical data and previous investigations carried out on complexes of this type, has shown that Cu^{+} is oxidised at a potential less positive than Ru^{2+} , and $\mathrm{Cu}^{\mathrm{II}}$ is interacting with $\mathrm{Ru}^{\mathrm{II}}$ through a cyanide bridge. Complex [7] shows similar behaviour.

2.5. Luminescence properties

Room temperature emission band maxima, lifetimes and luminescence quantum yields are reported in Table 5. Representative luminescence spectra are shown in Fig. 5. The absorption spectra of cyanobridged complexes are dominated by the Ru(bpy)²⁺₂ chromophoric unit and the contribution of [Cu(AsPh₃)(NN)]⁺ is negligible. Upon excitation performed at ~480 nm, these complexes exhibit emission band maxima at ~642 nm and are tentatively assigned as metal-to-ligand charge transfer transitions [36]. Besides these bands, emission bands appear at ~525–

545 nm. The assignment of these electronic excited states poses an interesting problem. Probably the emission occurs from a copper sub-unit. Copper(I) centre, a d¹⁰ system is very electron rich in nature and can be stabilised by lignads having π -acid character, viz. PPh₃, bpy, phen, CO, CN- etc. Complexes having general formula [Cu(PPh₃)₂(NN)]⁺, are known to exhibit emission properties both at low and room temperature. McMillin et al [33, 37]. observed emissions at 608 and 575 nm in [Cu(PPh₃)₂(phen)]⁺ and 620 nm in $[Cu(PPh_3)_2(bpy)]^+$. These emissions were tentatively assigned as metal-to-ligand charge transfers. However, a metal-centred $d \rightarrow s$ orbital transition was not ruled out. Moreover, there is extensive literature on the emission of poly nuclear copper(I) complexes. In the tri-nuclear copper(I) complex $[Cu_3(dpmp)_2(MeCN)_2(\mu - Cl)_2]^+$, where dpmp is bis(diphenylphosphinomethyl)methyl phosphine, an emission at 560 nm was assigned as a metal-centered $3d^94s^1 \rightarrow 3d^{10}$ transition [38]. In the bi-nuclear copper(I) complex [PPh₃Cu₂Cl₂(py)] a similar type of assignment has been made by Jink et al.[39]. However, the possibility of a CT excited state was also predicted.

The emission bands at ~525–545 nm in the complexes [4], [6] and [7] have been assigned, based on a literature assignment of analogous compounds and our experimental observation. The complex [4] undergoes bi-exponential decay showing lifetimes at 0.201 ns (A_1 =0.67) and 2.59 ns (A_2 =0.33), [Fig. 6]. This confirms the presence of two species in the excited state, namely the copper and ruthenium sub-units.

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Complex	$\lambda^{a}_{em}(nm)$	τ (ns)	ϕ	$K_{r}\left(s^{-1} ight)$	$K_{nr}\left(s^{-1} ight)$
[4]	642	0.201	6.7×10^{-3}	33×10^{6}	4.9×10^9
[6]	644	0.118	7.5×10^{-4}	6.3×10^{6}	8.4×10^9
[7]	641	0.110	1.5×10^{-4}	1.3×10^{6}	9.0×10^9

Table 5. Luminescence Properties at 298 K

a denotes Ru \rightarrow bpy MLCT excited states, other λ_{em} values are \sim 525–545 nm for [4], [6] and [7] are assigned as metal-centered and metal-to-ligand charge transfer excited states.



Fig. 5. Luminescence spectra of complexes [4], [6] and [7]; excitation were performed at $\lambda_{abs} \approx 480$ nm.

Hence the 525–545 nm emission bands have been assigned tentatively as metal-to-ligand charge transfers and metal-centred transitions. Thus the bridging between copper and ruthenium moieties introduces a new high energy state in the system. This proves that both the copper and ruthenium metal centres are emitters. It follows that energy transfer occurs from the ruthenium to the copper sub-unit due to ligand dissociation and the solvent (CH₃CN) takes the place of the copper coordination site [40]. Latimer type diagram of the complex [6] illustrate this inter-relationship using excited state redox potential in Fig. 7 in which oxidation of Cu(I) to Cu(II) occurs readily and hence

the excited states of Cu(I)–polypyridyl sub-unit are potentially strongly reductant [33].

On the basis of the above facts, lifetimes and emission intensities decrease in the order $(AsPh_3)_2 >$ $(phen)(AsPh_3) > (bpy)(AsPh_3)$ when $\lambda_{em} \approx 640$ nm, suggesting that non-radiative decay processes increase in efficiency along the same sequence and are significantly more effective in the bipyridine complex. These processes are also due to the favourable energetics of the bipyridine ligand bound to copper. The observation shows that the quantum efficiency of electron transfer is limited by the competing non-radiative decay process, which is quite rapid ($\approx 10^9 \text{ s}^{-1}$).



Fig. 6. Fluorescence decay curve of complex [4] at emission wavelength of 642 nm.



Fig. 7. Latimer type diagram showing ground and excited state potential of [6].

3. CONCLUSION

These studies show that the $[Ru(bpy)_2Cl]^+$ chromophore bound to copper moieties through a CN bridge cannot be easily functionalised. These moieties are redox active and ligand substitution usually causes a small change in excited state energy, but they can significantly change the excited state lifetime and the excited state redox potential. These excitations in the $[Ru(bpy)_2Cl]^+$ chromophore play a major role in determining the occurrence of specific intramolecular electron transfer processes.

Though the complexes exhibit relatively short lifetimes, compared to analogous complexes at room temperature, their desired properties may lead to the simple preparation of photochemical devices [41]. Studies in these directions are in progress.

Acknowledgements—The authors are grateful to Prof. T. K. Chandrashekar, Department of Chemistry, Indian Institute of Technology (Kanpur, India) and Prof. K. Bhattacharya and his group, Department of Physical Chemistry, Indian Association for the Cultivation of Science (Calcutta, India) for the use of the luminescence spectrophotometer and the lifetime measurement apparatus respectively. We gratefully acknowledge I.I.T. Delhi, India for the low frequency IR Spectra and Cyclic voltammogram data. The authors are grateful to Mr. H. M. Guniyal, CDRI, RSIC, Lucknow, for recording the ²D–NMR spectrum.

REFERENCES

- (a) Balzani, V., Moggi, L., Monfrin, M. F., Bolletta, F., Gleria, M., *Science*, 1975, **189**, 852;
 (b) Balzani, V., Bolletta, F., Gandolfi, M. and Maestri, M., *Top. Curr. Chem.*, 1978, **75**, 1; (c) Sutin, N. and Creutz, C., *Pure Appl. Chem.*, 1980, **52**, 2717; (d) Kalyanasundaram, K., *Coord. Chem. Rev.*, 1982, **46**, 159.
- (a) Balzani, V., Barigelletti, F. and Cola, L. D., Top. Curr. Chem., 1990, 158, 31; (b) Kalyanasundaram, K., Photochemistry of Polypyridine and Porphyrin Complexes. Academic Press, New York, 1992, p. 105.
- (a) Denti, G., Campagna, S., Sabatino, L., Serroni, S., Ciano, M. and Balzani, V., *Inorg. Chem.*, 1990, **29**, 4751; (b) Fagalde, F. and Katz, N. E., *J. Chem. Soc.*, *Dalton Trans.*, 1993, 571.
- (a) Scandola, F., Indelli, M. T., Chiorbolli, C., Bignozzi, A., *Top. Curr. Chem.*, 1990, **158**, 73 and refs therein; (b) Denti, G., Serroni, S., Campagna, S., Ricevuto, V., Juris, A., Ciano, M. and Balzani, V., *Inorg. Chim. Acta*, 1992, **198-200**, 507; (c) Denti, G., Campagna, S., Serroni, S., Ciano, M. and Balzani, V., *J. Am. Chem. Soc.*, 1992, **114**, 2944; (d) Bardwell, D. A., Barigelletti, F., Cleary, R. L., Flamigni, L., Guardigli, M., Jeffery, J. C. and Ward, M. D., *Inorg. Chem.*, 1995, **34**, 2438.
- 5. (a) Scandola, F., Bignozzi, C. A., Chiorboli, C.,

Indelli, M.T., Rampi, M.A., *Coord. Chem. Rev.*, 1990, **97**, 299 and refs. therein; (b) Bignozzi, C. A. and Scandola, F. A., *Inorg. Chem.*, 1984, **23**, 1540; (c) Carriedo, G. A., Connelly, N. G., Crespo, M. C., Duarmby, I. C., Riera, V. and Worth, G. H., *J. Chem. Soc.*, *Dalton Trans.*, 1991, 315; (d) Darensbourg, D. J., Yoder, J. C., Holtcamp, M. W., Klausmeyer, K. K. and Reibenspies, J. H., *Inorg. Chem.*, 1996, **35**, 4764.

- (a) Baird, G. J., Davies, S. G., Moon, S. D., Simpson, S. J. and Jones, R. H., J. Chem. Soc. Dalton Trans., 1985, 1479; (b) Christofides, A., Connelly, N. G., Lawson, H. J., Loyns, A. C., Orpen, A. G., Simmonds, M. O. and Worth, G. H., J. Chem. Soc. Dalton. Trans., 1991, 1595; (c) Laidlaw, W. M. and Denning, R. G., J. Chem. Soc. Dalton. Trans., 1994, 1987; (d) Laidlaw, W. M. and Denning, R. G., Polyhedron, 1994, 13, 1880 and 2337.
- 7. Singh, R. and Dikshit, S. K., *Polyhedron*, 1993, **12**, 1697.
- 8. Kutal, C., *Coord. Chem. Rev.*, 1990, **99**, 213 (and refs therein).
- Singh, R. and Dikshit, S. K., Chem. Educ., 1992, 9, 51.
- Sulivan, B. P., Salmon, D. J. and Meyer, T. J., *Inorg. Chem.*, 1978, **17**, 3334.
- Bruce, M. I., Hameister, C., Swincer, A. G. and Wallis, R. C., *Inorg. Synth.*, 1982, **21**, 78.
- 12. Reichle, W. T., Inorg. Chim. Acta., 1971, 5, 325.
- 13. Geary, W. J., Coord. Chem. Rev., 1971, 7, 81.
- Cooper, D. and Plane, R. A., *Inorg. Chem.*, 1966, 5, 2209.
- 15. Nakamoto, K., Infrared and Raman Spectra of Inorganic and Coordination Comounds, John Wiley, New York, 1986, 278.
- (a) Whiffen, D. H., J. Chem. Soc., 1956, 1350 (b) Shobatake, K., Postmus, C., Ferraro, J. R. and Nakamoto, K., Appl. Spectrosc., 1969, 23, 12. (c) Jones, A. G. and Powell, D. B., Spectrochim. Acta, 1974, 30A, 563. (d) Haines, R. J. and Dupreez, A. L., J. Organomet. Chem., 1975, 84, 357; Lippincott, E. R. and Welson, R. D., Spectrochim. Acta, 1958, 10, 307. (e) Edwards, H. G. M., Lewis, T. R. and Turner, P. H., Inorg. Chim. Acta, 1994, 216, 191.
- 17. Konya, K. and Nakamoto, K., Spectrochim. Acta, 1973, **29A**, 1965.
- Percy, G. C. and Thornton, D. A., J. Mol. Struct., 1972, 14, 313.
- Wilde, R. E., Srinivasan, T. K. K., J. Inorg. Nucl. Chem., 1974, 36, 323.
- 20. Saito, Y., Takemoto, J., Hutchinson, B. and Nakamoto, K., *Inorg. Chem.*, 1972, **11**, 2003.
- 21. Staniewicz, R. J., Hendriker, D. G. and Griffiths, P. R., *Inorg. Nucl. Chem. Lett.*, 1977, **13**, 467.

- (a) Mackey, K. M., Sowerby, D. B., Young, W. C., *Spectrochim. Acta*, 1968, **24A**, 611; (b) Jones, L. H., *J. Chem. Phys.*, **29**, 1958, 463.
- (a) Wilezewski, T., Bochenska, M. and Niernet, J. F., J. Organomet. Chem., 1981, 215, 87; (b) Blackmore, T., Bruce, M. I. and Stone, F. G. A., J. Chem. Soc. (A)., 1971, 2376.
- Prasad, R., Mishra, L. and Agarwala, U.C., *Ind. J. Chem.*, 1991, **30A**, 45<comment>also 162 and refs. therein.
- (a) Constable, E. C. and Holmes, J. M., *Inorg. Chim. Acta.*, 1987, **126**, 195; (b) Kelly, J. M., O'Connell, C. M. and Vos, J. G., *J. Chem. Soc. Dalton Trans.*, 1986, 253.
- Heijden, M., Van Vliet, P. M., Haasnoot, J. G. and Reedijk, J., J. Chem. Soc., Dalton Trans., 1993, 3675.
- 27. Birchel, J. D., O'Donoghue, T. D. and Wood, J. R., *Inorg. Chim. Acta*, 1979, **37**, L461.
- 28. Singh, R. and Dikshit, S. K., *Polyhedron*, 1995, **14**, 1799 (and refs. therein).
- Bruce, M. I., Catlow, A., Humphery, M. G., Coutsantonis, G. A., Snow, M. R. and Tiekink, E. R. T., J. Organomet. Chem., 1988, 388, 59.
- Fergusson, J. E. and Harris, G.M., J. Chem. Soc. (A), 1966, 1293.
- Bryant, G. M., Fergusson, J. E. and Powell, H. K. G., Aust. J. Chem., 1971, 24, 257.
- 32. Cutin, E. H. and Katz, N. E., *Polyhedron*, 1993, **12**, 955.
- 33. Rader, A., McMillin, D. R., Buckner, T., Matthews, G., Casadonte, J., Lengel, K., Whittaker, B., Darmon, M. and Lytle, E., J. Am. Chem. Soc., 1981, 103, 3906.
- Brauenstein, C. H., Baker, A. D., Strekas, T. C. and Gafney, H. D., *Inorg. Chem.*, 1984, 23, 857.
- Hadjikakou, S. K., Akrivos, P. D., Karagiannidis, P. and Papadopoulos, N., *Polyhedron*, 1995, 14, 2999.
- Nakamaru, K., Bull. Chem. Soc. Jpn., 1982, 55, 2697.
- 37. (a) Buckner, M. T., Matthews, T. J., Lytle, F. E. and McMillin, D. R., *J. Am. Chem. Soc.*, 1979, 101, 7863; (b) Blasse, G. and McMillin, D. R., *Chem. Phys. Lett.*, 1980, 70, 1.
- Li, D., Yip, H. K., Che, C. M., Zhou, Z. Y., Mak, T. C. W. and Liu, S. T., J. Chem. Soc., Dalton Trans., 1992, 2445.
- Henry, M., Wotton, J. L., Khan, S. I. and Zink, J. I., *Inorg. Chem.*, 1997, 36, 796.
- Kalyanasundaram, K., Photochemistry of Polypyridine and Porphyrin Complexes, Academic Press, New York, 1992, p. 293.
- 41. Balzani, V., Moggi, L. and Scandola, F., *Supra-molecular Photochemistry*, Riedel, The Netherland, 1987.