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Notes

Influence of the Inner Coordination Sphere on the Ru(III)−Cyanamido Ligand-to-Metal Charge Transfer Chromophore

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Introduction

The extensive π conjugation between the cyanamide group and the phenyl ring provides an energetically favorable means by which a metal ion can couple into a conjugated organic π system. This has been experimentally demonstrated by the extraordinary ability of 1,4-dicyanamidobenzene to mediate metal−metal coupling in dinuclear ruthenium mixed-valence complexes,[1] and the wealth of data provided by the study of these systems has permitted a quantitative evaluation of metal−metal coupling within the context of Marcus−Hush theory.[2] The recent interest in the field of inorganic chemistry to develop novel hybrid materials that combine coordination and organic chemistry provides further impetus to this research.

In this study, we have synthesized and characterized the complexes [Ru(bpy)(trpy)L]$^+$ where trpy is 2,2′:6′,2″-terpyridine, bpy is 2,2′-bipyridine, and L is 4-methyl-, 3-chloro-, 2,4-dichloro-, 2,4,5-trichloro-, 2,4,6-trichloro-, 2,3,4,5-tetrachloro-2,3,5,6-tetrachloro-, or pentachlorophenylcyanamido anion ligand. Spectroelectrochemical oxidation to the Ru(III) complexes permitted an analysis of their Ru(III)−cyanamide ligand-to-metal charge transfer (LMCT) spectral properties and metal−ligand coupling elements in comparison to their pentaammineruthenium(III) analogues.[3]

Experimental Section

Equipment. UV−vis spectroscopy was perfomed on a CARY 5 UV−vis−NIR spectrophotometer. IR spectra were taken with a BOMEM Michelson-100 FT-IR spectrophotometer as KBr disks. The instrumentation used to perform cyclic voltammetry and spectroelectrochemistry has been described previously.[4]

Materials. All reagents and solvents used were reagent grade or better. Tetrabutylammonium hexafluorophosphate (TBAH) was purchased from Aldrich and recrystallized twice from ethanol/water and then vacuum-dried at 110 °C. Syntheses of [Ru(bpy)(trpy)Cl][PF$_6$][5] and the thallium salts of phenylcyanamide ligands (pcyd$^-$) have been previously described.[6] *Caution*: Thallium is toxic.

Complex preparations were very similar, and so only one example is shown below. Experimental details, elemental analyses, IR, and ^{1}H NMR data for the other complexes are in the Supporting Information.

Preparation of [Ru(bpy)(trpy)(4-Mepcyd)][PF$_6$]·DMF. [Ru(bpy)(trpy)Cl][PF$_6$] (0.34 g, 0.51 mmol) was dissolved in 25 mL of *N,N′* dimethylformamide (DMF) in a 50 mL round-bottom flask. Tl$^+$[4-Mepcyd]$^-$ (0.17 g, 0.51 mmol) was added, and the deep-red solution was refluxed for 18 h. The reaction mixture was then chilled to −20 °C and filtered to remove a fine white TlCl precipitate. The crude product precipitated as a deep-red-brown solid with the addition of 500 mL of ether to the filtrate and was collected by suction filtration. Recrystallization was achieved by the slow diffusion of ether into a saturated solution of the crude complex in DMF. Yield: 0.29 g (76%). ν(NCN): 2156 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): 9.63(d, 1H), 8.87(d, 1H), 8.80(d, 2H), 8.68(d, 2H), 8.61(d, 1H), 8.35(t, 1H), 8.23(t, 1H), 8.03(m, 3H), 7.80(t, 1H), 7.68(d, 2H), 7.41(m, 3H), 7.11(t, 1H), 6.58(d, 2H), 5.82(d, 2H). Anal. Calcd for [Ru(bpy)(trpy)(4-Mepcyd)][PF$_6$]·DMF ($C_{36}H_{33}N_8OPF_6Ru$): C, 51.49; H, 3.96; N, 13.34. Found: C, 51.03; H, 3.95; N, 13.22.

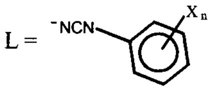
Oscillator Strength Calculation. The approach used for non-Gaussian band shapes has been previously described.[7] A figure showing the fitting procedure on the low-energy LMCT band of [Ru(bpy)(trpy)(2,3,4,5-Cl$_4$pcyd)]$^{2+}$ has been placed in the Supporting Information.

Crystallography. Crystals of [Ru(bpy)(trpy)(2,4-Cl$_2$pcyd)]PF$_6$·DMF were grown by ether diffusion into a DMF solution of the complex. The data were collected on a 1K Siemens Smart CCD using Mo Kα radiation (λ = 0.710 73 Å) at 238(2) K using an ω-scan technique and corrected for absorptions using equivalent reflections.[8] No symmetry higher than triclinic was observed, and solution in the centric space group option yielded chemically reasonable and computationally stable results of refinement. The structure was solved by direct methods and refined with full-matrix least-squares procedures. Anisotropic refinement was performed on all non-hydrogen atoms. All hydrogen atoms were calculated. Scattering factors are contained in the SHELXTL 5.1 program library.

Results

The Ru(II) complexes were synthesized in generally good yields according to the following metathesis reaction in refluxing DMF.

$$[\mathrm{Ru(bpy)(trpy)Cl}]^+ + \mathrm{Tl}^+\mathrm{L}^- \rightarrow [\mathrm{Ru(bpy)(trpy)L}]^+ + \mathrm{TlCl}\downarrow$$



Under these conditions, the cyanamide group preferentially binds to Ru(II) through the nitrile nitrogen instead of the amide nitrogen as shown by the crystal structure discussed below. A previous ^{1}H NMR study of the reaction of phenylcyanamide ligands with Ru(II) 2,6-bis(1-methylbenzimidazol-2-yl)pyridine complexes indicated that the amide bound linkage isomer

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Table 1. Crystal Data and Structure Refinement for $[Ru(bpy)(trpy)(2,4\text{-}Cl_2pcyd)]PF_6{\cdot}DMF$

formula	$C_{35}H_{29}F_6Cl_2N_8OPRu$	fw	894.60
space group	$P1$	Z	2
cryst syst	triclinic	D_c, Mg/m^3	1.593
a, Å	11.681(4)	α, deg	68.00 (2)
b, Å =	12.240(5)	β, deg	70.05 (3)
c, Å	15.017(5)	γ, deg	78.55 (2)
V, Å^3	1865(1)	temp, K	238 (2)
R1^a	0.0722	G_{of} on F^2	1.100
wR2^b	0.2122		

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR2 = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

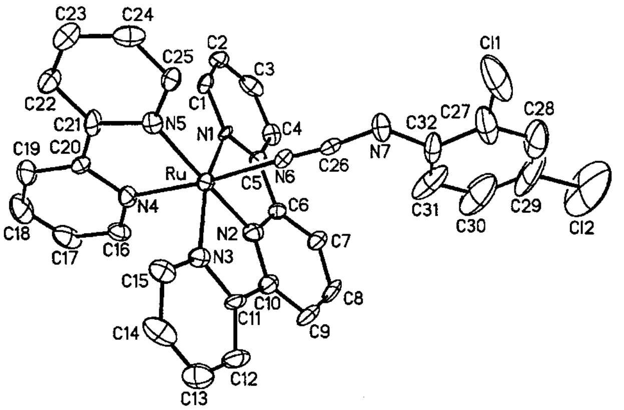

Figure 1. ORTEP drawing of $[Ru(bpy)(trpy)(2,4\text{-}Cl_2pcyd)]PF_6$. DMF. The counterion and solvent of crystallization have been omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Ru−N(1), 2.076(8); Ru−N(6), 2.088(7); Ru−N(2), 1.962(9); N(6)−C(26), 1.132(10); Ru−N(3), 2.084(8); N(7)−C(26), 1.288(10); Ru−N(4), 2.035(6); N(7)−C(32), 1.437(10); Ru−N(5), 2.076(8); N(1)−Ru−N(2), 79.7(4); N(4)−Ru−N(5), 78.7(3); N(1)−Ru−N(5), 98.8(3); N(6)−C(26)−N(7), 171.5(10); N(2)−Ru−N(3), 79.4(3); C(26)−N(7)−C(32), 119.6(8); N(3)−Ru−N(4), 91.4(3); C(26)−N(6)−Ru, 169.0(6).

formed initially but at ambient temperatures slowly converted to the nitrile nitrogen bound linkage isomer.[9]

Deep-brown, almost black, crystalline shards of $[Ru(bpy)(trpy)(2,4\text{-}Cl_2pcyd)]PF_6{\cdot}DMF$ were grown by DMF/ether diffusion. Crystal data and selected bond lengths and angles appear in Table 1 and in the caption of Figure 1, respectively. An ORTEP drawing of the complex is shown in Figure 1. The Ru(II) ion occupies a pseudo-octahedral coordination sphere of nitrogen donor atoms where the cyanamide group of the phenylcyanamide ligand is trans to a pyridine moiety of the bipyridine ligand. The cyanamide group is approximately linear (171.5(10)°) as is the angle describing the coordination of its terminal nitrogen to Ru(II) (169.0(6)°). Similar bond angles have been observed when phenylcyanamides coordinate to Ru(III) ions.[3,10] The Ru(II)−NCN bond length was measured at 2.088 (7) Å and is somewhat larger than that found in the crystal structure of *trans*-$[Ru(pyridine)_4(2\text{-}Clpcyd)_2]$, with Ru(II)−cyanamide bond lengths of 2.041 (6) and 2.060 (6) Å.[4] The Ru(II)−cyanamide bond is considerably larger than the average Ru(III)−cyanamide bond length of 1.97 (2) Å that was derived from six Ru(III)−cyanamide structures[3,10] and can be attributed to the effect of the ruthenium oxidation state.

Cyclic voltammetry data for the $[Ru(bpy)(trpy)L]^+$ complexes are given in Table 2, and a representative voltammogram of $[Ru(bpy)(trpy)(2,4\text{-}Cl_2pcyd)]PF_6$ appears in Supporting Information. The Ru(III/II) couples are quasi-reversible and generally possess invariant anodic to cathodic peak separations of 80 mV at scan rates between 50 and 500 mV/s in acetonitrile. The phenylcyanamide L(0/−) couples are significantly less reversible, having much larger peak-to-peak separations and greater sensitivity to scan rate. At negative potential, waves associated with the reduction of bpy and trpy ligands overlap (Table 2), making assignment difficult. Nevertheless, the trpy reduction wave has been suggested to occur at the most positive potential because of the greater stability of its π^* orbitals.[11]

The electronic spectral data of the $[Ru(bpy)(trpy)L]PF_6$ complexes in acetonitrile solution are given in Table 3, and a figure showing the absorption spectrum of $[Ru(bpy)(trpy)(2,4\text{-}Cl_2pcyd)][PF_6]$ in acetonitrile has been placed in Supporting Information. Spectroscopic assignments were made by comparison to the literature.[12]

Spectroelectrochemistry was performed on these complexes in order to generate the Ru(III) spectra and in turn allow the study of the spectral data associated with the Ru(III)−cyanamide LMCT chromophore. The low-energy LMCT band data have also been placed in Table 3, and a representative visible spectrum showing the electrochemical generation of the $[Ru(bpy)(trpy)(2,3,4,5\text{-}Cl_4pcyd)]^{2+}$ ion in acetonitrile solution is given in Figure 2. A previously published spectroscopic analysis[6,7] of the Ru(III)−cyanamide LMCT chromophore of $[Ru(NH_3)_5L]^{2+}$ assumed C_{4v} microsymmetry about Ru(III) and is applicable to the $[Ru(bpy)(trpy)L]^{2+}$ complexes of this study. Accordingly, in Figure 2, the low-energy LMCT band at 1058 nm is assigned to the $b_1 \rightarrow b_1^*$ transition while the high-energy LMCT band at 430 nm is assigned to the formally forbidden $b_2 \rightarrow b_1^*$ transition.

Discussion

By comparison of the Ru(III/II) couples of analogous $[Ru(NH_3)_5L]^{2+}$ and $[Ru(bpy)(trpy)L]^+$ complexes in Table 2, an approximately 0.8 V positive shift in potential occurs upon the replacement of ammine ligands with pyridine moieties. This is a consequence of pyridine's relatively poor σ-donor properties and its π-acceptor properties when bonded to Ru(II). From the difference between analogous $[Ru(NH_3)_5L]^{2+}$ and $[Ru(bpy)(trpy)L]^{2+}$ L(0/−) couples (Table 2), it can be seen that the effect of the more electropositive Ru(III) ion on the L(0/−) couples is smaller, resulting in an approximately 0.2 V positive shift in potential.

It has been known for many years that it is possible to correlate charge-transfer band energies to the difference in redox couples between the centers involved in the charge-transfer event.[13] The equation dealing specifically with LMCT transitions[14] is

$$E_{\mathrm{LMCT}} = [\mathrm{L}(0/-) - \mathrm{Ru(III/II)} + C] + \chi \qquad (1)$$

where E_{LMCT} is the LMCT energy in eV, C is a correction to account for the experimental impossibility of measuring the Ru-

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Table 2. Electrochemical Data[a] for $[Ru(bpy)(trpy)L]^+$ and $[Ru(NH_3)_5L]^{2+}$ Complexes in Acetonitrile

L	$[Ru(bpy)(trpy)L]^+$ Ru(III/II)	$[Ru(bpy)(trpy)L]^+$ L(0/−)	bpy or trpy couples			$[Ru(NH_3)_5L]^{2+}$ [c] Ru((III/II)	$[Ru(NH_3)_5L]^{2+}$ [c] L(0/-1)
4-Mepcyd$^-$	0.81[b]		−1.10	−1.38	−1.57	0.04	1.16
3-Clpcyd$^-$	0.93[b]		−1.11	−1.36	−1.59	0.12	1.47[b]
2,4-Cl_2pcyd$^-$	1.00	1.64	−1.10	−1.36	−1.61	0.15	1.44
2,4,5-Cl_3pcyd$^-$	1.06	1.75	−1.06	−1.31	−1.57	0.20	1.54
2,4,6-Cl_3pcyd$^-$	1.03	1.74	−1.03	−1.28	−1.64	0.13	1.50
2,3,4,5-Cl_4pcyd$^-$	1.09	1.81	−1.09	−1.29	−1.59	0.23	1.63
2,3,5,6-Cl_4pcyd$^-$	1.08	1.83	−1.06	−1.31	−1.56	0.21	1.69[b]
Cl_5pcyd$^-$	1.09	1.85	−1.10	−1.37	−1.66	0.23	1.67

[a] In volts vs NHE at 25 °C and a scan rate of 0.1 V/s; 0.1 M TBAH; ferrocene ($Fc^+/Fc = 0.665$ V vs NHE) was used as an internal reference. [b] Irreversible wave, anodic peak only. [c] From ref 4 and corrected for an old calibration value of $Fc^+/Fc = 0.400$ V vs NHE.

Table 3. Electronic Spectroscopy Data[a] for $[Ru(bpy)(trpy)L]^+$ Complexes and the Ru(III) LMCT Spectral Data of the $[Ru(bpy)(trpy)L]^{2+}$ Complexes in Acetonitrile

L	$\pi \rightarrow \pi^*$	MLCT	LMCT
4-Mepcyd$^-$	239 (3.32), 278 (4.78), 291 (4.25), 315 (3.41)	496 (0.736)	N/A[b]
3-Clpcyd$^-$	237 (3.23), 281 (5.09), 290 (4.65), 314 (3.76)	494 (0.839)	N/A[b]
2,4-Cl_2pcyd$^-$	237 (3.22), 282 (5.22), 290 (5.29), 314 (3.96)	492 (0.835)	1144[c]
2,4,5-Cl_3pcyd$^-$	282 (4.89), 291 (5.37), 314 (4.10)	489 (0.844)	1073[c]
2,4,6-Cl_3pcyd$^-$	282 (4.62), 292 (5.19), 315 (4.18)	495 (0.859)	1071 (0.913)[d]
2,3,4,5-Cl_4pcyd$^-$	282 (4.67), 291 (5.20), 313 (4.37)	487 (0.866)	1058 (1.16)[d]
2,3,5,6-Cl_4pcyd$^-$	220 (5.80), 282 (4.26), 292 (4.85), 315 (4.33)	490 (0.859)	1009 (0.811)[d]
Cl_5pcyd$^-$	224 (6.15), 282 (4.37), 291 (5.00), 314 (4.39)	489 (0.849)	1038 (0.826)[d]

[a] λ_{max} in nm; $\epsilon/10^4$ M^{-1} cm^{-1} in parentheses. [b] The stability of the Ru(III) complex was so poor that isosbestic points could not be observed. [c] The formation of the Ru(III) complex gave well-defined isosbestic points; however, reversibility was no better than 80%. [d] Very good reversibility (>95%) in regenerating the Ru(II) spectra.

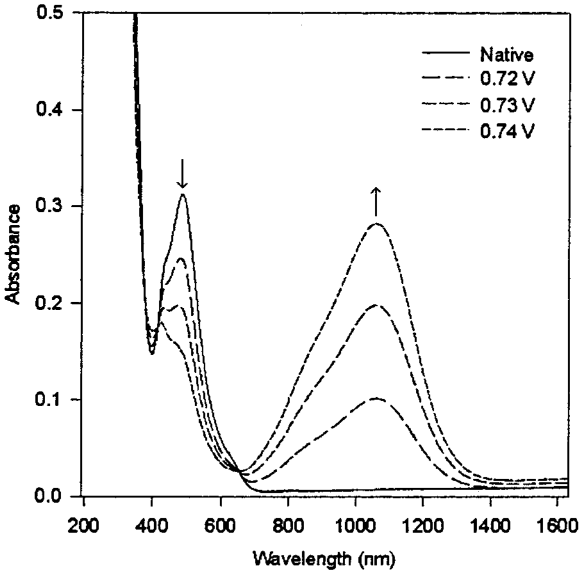

Figure 2. Optically transparent thin-layer electrode cell electronic spectra of $[Ru(bpy)(trpy)(2,3,4,5\text{-}Cl_4pcyd)]^{1+/2+}$ in acetonitrile under increasing oxidation potentials: 0.1 M TBAH; gold foil working and counter electrodes; silver/silver chloride wire reference electrode.

(III/II) couple when the oxidized ligand L^0 is bonded to Ru(III), and χ is the term used to account for the population of excited vibrational levels of the LMCT excited state. The magnitude of χ is determined by the inner- and outersphere reorganizational energies of the complex.[14] A plot of E_{LMCT} vs L(0/−) − Ru(III/II), using the data in Tables 2 and 3, does give a linear correlation with slope 1.01, intercept 0.45, and square of the correlation coefficient 0.99 (see Supporting Information). While C for both families of complexes might be considered the same, the value of χ should not because both inner- and outersphere reorganizational energies are expected to be significantly different for the two families of complexes.[15]

Table 4: LMCT Oscillator Strengths[a] and Metal−Ligand Coupling Elements[b] Derived from the $b_1 \rightarrow b_1^*$ LMCT Transition of Bipyridine(terpyridine)ruthenium(III) and Pentaammineruthenium(III) Phenylcyanamide (pcyd$^-$) Complexes

L	$[Ru(bpy)(trpy)L]^{2+}$ f	$[Ru(bpy)(trpy)L]^{2+}$ H_{LM}	$[Ru(NH_3)_5L]^{2+}$ f	$[Ru(NH_3)_5L]^{2+}$ H_{LM}
2,4-Cl_2pcyd$^-$			0.156	2540
2,4,5-Cl_3pcyd$^-$			0.148	2520
2,4,6-Cl_3pcyd$^-$	0.152	2050	0.128	2380
2,3,4,5-Cl_4pcyd$^-$	0.183	2270	0.119	2280
2,3,5,6-Cl_4pcyd$^-$	0.153	2120	0.111	2270
Cl_5pcyd$^-$	0.178	2260	0.126	2410

[a] In acetonitrile solutions. [b] Calculated by using eq 2, $r = 5.56$ Å, and E_{LMCT} from Table 3, in cm^{-1}.

When the inner coordination sphere is changed from ammine to pyridine moieties, the Ru(III)−cyanamide LMCT chro-mophore energy decreases by approximately 0.6 eV, in agreement with the changes seen in the Ru(III/II) and L(0/−) couples. This should result in greater covalency in the Ru(III)−cyanamide bond, and because the Ru(III) ion is more electropositive, the bond should be stronger. Creutz, Newton, and Sutin[16] have shown that it is possible to calculate metal−ligand coupling elements H_{LM} from charge-transfer spectral data by using

$$H_{LM} = \frac{3.03 \times 10^2}{r} (E_{LMCT} f)^{1/2} \tag{2}$$

where r is the transition dipole moment length in Å, E_{LMCT} is the LMCT band energy in cm^{-1} at ϵ_{max}, and f is the oscillator

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(15) The possibility that the differences between both inner- and outersphere reorganizational energies fortuitously cancel out was explored by solvent studies. Unfortunately, the $[Ru(bpy)(trpy)L]^+$ complexes were only soluble in high dielectric solvents and the inability to examine the redox properties of these complexes in a range of solvent properties prevented a definitive statement on outersphere contributions to χ.

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strength of the LMCT band. This expression is identical in form to that derived by Hush to determine metal−metal coupling elements from intervalence band oscillator strengths.[2] We used this formula to calculate the H_{LM} associated with the Ru(III)−cyanamide LMCT transition for both $[Ru(bpy)(trpy)L]^{2+}$ and $[Ru(NH_3)_5L]^{2+}$ complexes (see Table 4), assuming an estimated transition dipole moment length for phenylcyanamide ligands of 5.56 Å.[7] The H_{LM} values for $[Ru(NH_3)_5L]^{2+}$ are significantly larger than those determined for $[Ru(bpy)(trpy)L]^{2+}$, suggesting that the Ru(III)−cyanamide dπ bonding in $[Ru(bpy)(trpy)L]^{2+}$ has decreased as Ru(III) d orbitals become more stabilized. A rigorous theoretical analysis may indicate whether this has occurred, and electroabsorption spectroscopy should reveal the appropriate dipole moment length to apply to eq 2. We hope to pursue these studies in the future.

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Supporting Information Available: Four figures showing the quantitative electronic spectrum of $[Ru(bpy)(trpy)(2,4\text{-}Cl_2pcyd)]PF_6$, the best fit of three Gaussian curves to the $b_1 \rightarrow b_1^*$ LMCT band of $[Ru(bpy)(trpy)(2,3,4,5\text{-}Cl_4pcyd)]^{2+}$, cyclic voltammogram of $[Ru(bpy)(trpy)(2,4\text{-}Cl_2pcyd)]PF_6$, and a plot of E_{LMCT} versus L(0/−) − Ru(III/II); experimental details, elemental analyses, IR and ^{1}H NMR data for the complexes; full listings of crystal structure data, tables of atomic parameters, anisotropic thermal parameters, bond lengths, bond angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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