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Journal of Molecular Structure 740 (2005) 165–168
Journal of MOLECULAR STRUCTURE
www.elsevier.com/locate/molstruc

Synthesis, structure and spectroscopic study of Rh^{III} polypyridine complexes with phenylcyanamide derivative ligands

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Received 4 January 2005; revised 23 January 2005; accepted 24 January 2005

Abstract

Several new Rh^{III} complexes, $[Rh(tpy)(bpy)L](PF_6)_2$ (tpy = 2,2′:6′,2″-terpyridine, bpy = 2,2′-bipyridine, and L = monoanions of phenylcyanamide(pcyd)), 4-methylphenylcyanamide (4-MePcyd), 2,4-dimethylphenylcyanamide (2,4-Me_2pcyd), 4-methoxyphenylcyanamide (4-MeOPcyd), 2-chlorophenylcyanamide (2-Clpcyd) and 2,5-dichlorophenylcyanamide (2,5-Cl_2pcyd) have been synthesized and characterized by elemental analysis, IR, ^{1}H NMR and electronic absorption spectroscopies. ORTEP drawing of $[Rh(tpy)(bpy)(2,5\text{-}Cl_2pcyd)](PF_6)_2 \cdot 1/2CH_3CN$ shows three pyridyl rings of the tpy ligand that are nearly coplanar, as are the two rings of bpy. The anionic cyanamide group is coordinated end-on by the nitrile nitrogen to the Rh^{III}. The Rh^{III}–NCN bond is bent, having an angle of 125.4°. This bent bond is largely determined by the σ-bonding interaction of a cyanamide non-bonding electron pair in a sp^2 hybrid orbital.

Keywords: Rh^{III} complex; Phenylcyanamide ligand; Polypyridyl ligand; Metal to ligand charge-transfer; Crystal structure; Pseudohalides

1. Introduction

Phenylcyanamide coordination chemistry has been the subject of a recent review [1]. Phenylcyanamide ligands are pseudohalides. However, the attachment of a phenyl ring to the cyanamide group (NCN) adds an extra dimension not present in azide or thiocyanate ligands. An 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 [1]. The coordination chemistry of phenylcyanamide ligands still requires much effort to complete. At this point in time, only the crystal structures of Ru^{II}, Ru^{III}, Ni^{II}, Pd^{II}, Cu^{II}, Cu^{I}, Ag^{I} and Co^{III} phenylcyanamide complexes have been obtained [2–15]. In this study, a series of novel mononuclear complex of $[Rh(tpy)(bpy)L](PF_6)_2$, where L = a phenylcyanamide anion ligand, have been synthesized and characterized by elemental analysis, IR, ^{1}H NMR and electronic absorption spectroscopies. A crystal structure determination of the complex $[Rh(tpy)(bpy)(2,5\text{-}Cl_2pcyd)](PF_6)_2$ has been performed and compared with the structures of other transition metal complexes of phenylcyanamide ligands.

2. Experimental

2.1. Materials and general methods

All reagents and solvents used were reagent grade or better. $[Rh(tpy)(bpy)Cl](PF_6)_2$ [16] and the thallium salts of phenylcyanamide ligands [17] were synthesized according to literature procedures. Caution: Thallium is toxic.

Elemental analyses were performed by Heraeus CHN–O-Rapid elemental analyzer. IR spectra were measured on a Shimadzu 460 spectrophotometer with KBr pellets and electronic spectra on a JASCO 7850 spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker DRX-500 MHz AVANCE spectrometer at ambient temperature in DMSO-d_6.

2.2. Syntheses of the complexes

Complex preparations were very similar, and so only general method is shown below. A mixture of $[Rh(tpy)(bpy)Cl](PF_6)_2$ (1 mmol) and deprotonated

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doi:10.1016/j.molstruc.2005.01.051

Table 1
Analytical data for $[Rh(tpy)(bpy)L](PF_6)_2$ complexes

[Rh(tpy)(bpy)-L]$(PF_6)_2$, L	Anal. calc. and found (%)			Yield (%)
	C	H	N	
pcyd	42.73	2.69	10.90	84
	42.97	2.76	11.02	
4-Mepcyd	43.39	2.87	10.73	79
	43.52	2.99	10.97	
2,4-Me_2pcyd	44.03	3.04	10.57	75
	44.38	3.12	10.88	
4-MeOpcyd	42.65	2.82	10.55	86
	42.77	2.87	10.73	
2-Clpcyd	41.16	2.48	10.50	80
	41.30	2.57	10.86	
2,5-Cl_2pcyd	39.70	2.29	10.13	73
	40.05	2.34	10.30	

phenylcyanamide (thallium salt) (1 mmol) dissolved in 25 ml of *N*,*N*′-dimethylformamide (DMF) was stirred at reflux temperature overnight. The resulting reaction mixture was allowed to cool to room temperature and then left in a refrigerator overnight. The white solid (TlCl) was filtered off. The crude product precipitated as a yellow-orange solid with the addition of 200 ml of diethylether to the filtrate and was collected by suction filtration. Recrystallization was achieved by the slow diffusion of diethylether into a saturated solution of the crude complex in CH_3CN. The analytical data for the Rh^{III} complexes are collected in Table 1.

2.3. X-ray crystallographic study of $[Rh(tpy)(bpy)(2,5\text{-}Cl_2pcyd)](PF_6)_2 \cdot 1/2CH_3CN$

Yellow crystals of $[Rh(tpy)(bpy)(2,5\text{-}Cl_2pcyd)](PF_6)_2 \cdot 1/2CH_3CN$ were grown by ether diffusion into an acetonitrile solution of the complex. Single-crystal X-ray diffraction measurements were carried out with a BRUKER AXS SMART 2K/platform diffractometer equipped with a graphite monochromator for data collection at 220(2) K. The determination of unit cell dimensions and data collection was performed with Cu Kα radiation ($\lambda = 1.54178$ Å). Data reduction processing was carried out by the use of the program SAINT [18], which applied Lorentz and Polarization corrections to three-dimensionally integrated diffraction spots. The program SADABS [19] was utilized for the scaling of diffraction data, the application of a decay correction, and an empirical absorption correction based on redundant reflections.

The space group was confirmed by XPREP routine in SHELXTL program [20]. The structure was solved by direct method using SHELXS97 [21] and difmap synthesis using SHELXL97 [22]. All non-H atoms anisotropic, hydrogen atoms isotropic. H atoms constrained to the parent site using a riding model; SHELXL97 defaults, C–H 0.94 to 0.97 Å. The isotropic factors, U_{iso}, were adjusted to 50% higher value of the parent site(methyl) and 20% higher (others). A final verification of possible voids was performed using the VOID routine of the PLATON program [23]. Further details of the structural analyses are given in Table 2. Selected bond lengths and angles are listed in Table 3.

Table 2
Crystallographic data and structure refinement summary for $[Rh(tpy)(bpy)(2,5\text{-}Cl_2pcyd)](PF_6)_2 \cdot 1/2CH_3CN$

Formula	$C_{33}H_{23.5}Cl_2F_{12}N_{7.5}P_2Rh$
Molecular weight	988.84
Crystal system	orthorhombic
Space group	*Fdd2*
Unit cell dimensions (Å)	$a = 84.228(3)$
	$b = 8.7162(3)$
	$c = 21.4921(7)$
Volume (Å^3)	15,778.4(9)
Z	16
D_{calcd} (g/cm^3)	1.665
μ (mm^{-1})	6.368
Crystal size (mm)	$0.45 \times 0.14 \times 0.03$
Range of h, k, l	$-90/89$, $-9/9$, $-22/22$
Reflections collected/unique	48,988/4971
Parameters	713
R and R_w	0.0644, 0.1752
Residual electron densities (e/Å^3)	1.489 to -0.957
Goodness of fit	1.051

3. Results and discussion

The Rh^{III} complexes were synthesized in generally good yields according to the following metathesis reaction in refluxing DMF.

$$[Rh(tpy)(bpy)Cl](PF_6)_2 + Tl^+L^- \rightarrow [Rh(tpy)(bpy)L] \times (PF_6)_2 + TlCl\downarrow$$

L = monoanion of phenylcyanamide ligands

Under these conditions, the cyanamide group preferentially binds to Rh^{III} through the nitrile nitrogen instead of the amide nitrogen as shown by the crystal structure discussed

Table 3
Selected bond length (Å) and angles (deg) for $[Rh(tpy)(bpy)(2,5\text{-}Cl_2pcyd)](PF_6)_2 \cdot 1/2CH_3CN$

Bond lengths			
Rh–N(18)	1.942(8)	Rh–N(114)	2.057(8)
Rh–N(28)	2.013(9)	Rh–N(11)	2.065(8)
Rh–N(21)	2.046(7)	Rh–N(31)	2.068(9)
Bond angles			
N(18)–Rh–N(28)	97.4(4)	N(28)–Rh–N(31)	175.4(3)
N(18)–Rh–N(21)	176.7(3)	N(21)–Rh–N(31)	96.2(3)
N(28)–Rh–N(21)	79.3(3)	N(114)–Rh–N(31)	89.6(4)
N(18)–Rh–N(114)	80.8(3)	N(11)–Rh–N(31)	88.1(4)
N(28)–Rh–N(114)	90.4(3)	C(12)–N(11)–C(16)	121.6(9)
N(21)–Rh–N(114)	98.6(3)	C(12)–N(11)–Rh	127.0(7)
N(18)–Rh–N(11)	80.6(3)	C(16)–N(11)–Rh	111.3(6)
N(28)–Rh–N(11)	93.3(3)	C(19)–N(18)–Rh	119.0(6)
N(21)–Rh–N(11)	100.0(3)	C(17)–N(18)–Rh	118.0(6)
N(114)–Rh–N(11)	161.4(3)	C(32)–N(33)–C(34)	122.60(14)
N(18)–Rh–N(31)	87.1(4)	N(31)–C(32)–N(33)	175.30(11)