X-ray Structure of a Ruthenium Dinuclear Complex Incorporating 4,4′-Bis(cyanamidophenylethynyl)benzene as a Ligand, a Conjugated Bridge Two Nanometers in Length

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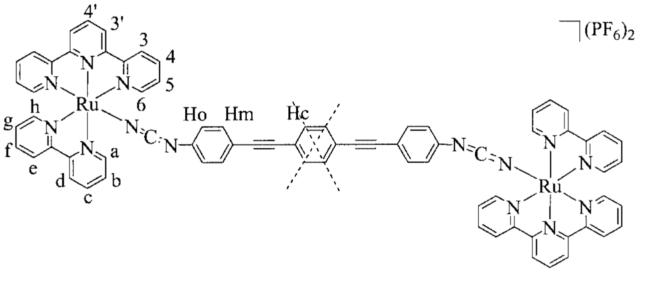
The reaction of $[Ru(bpy)(tpy)(Ipcyd)]^+$ (bpy = 2,2′-bipyridine, tpy = 2,2′:6′,2′′-terpyridine, Ipcyd = 4-iodophenylcyanamide anion) with diethynylbenzene in a Sonogashira cross-coupling reaction gives an unprecedentedly long and conjugated dinuclear complex $[\{[Ru(bpy)(tpy)]_2(\mu\text{-dcpeb})\}(BPh_4)_2]\cdot 4(PhCH_3)$ (dcpeb = dicyanamidophenylethynylbenzene dianion). The crystal structure data are as follows: crystal system monoclinic, space group $P2_1/c$, with a = 12.6960(3), b = 34.0960(10), c = 15.3540(4) Å, β = 110.7381(15)°, V = 6215.8(3) Å^3, and Z = 2. The structure was refined to a final R factor of 0.063. The metal ions are separated by a through-space distance of 24.9 Å.

Introduction

This work concerns the general theme of long distance electronic communication, a topic that is very important in biology[1] and also in molecular electronics.[2] One of our major preoccupations is to find a way to measure the electronic communication between redox sites through a molecular bridge (molecular wire), when the distance between these sites is long enough (>25 Å). Several methods may be followed. One such method was proposed by Crutchley, who found that NCN groups can be very efficient in ensuring a good communication between ruthenium atoms,[3] either in the mixed-valence state, by measuring the electronic coupling parameter (V_{ab}) using optical absorption techniques,[4] or in the homovalent state, by the magnetic exchange parameter (J) using magnetic susceptibility or EPR spectroscopy.[5] Following this line, we recently synthesized a mononuclear ruthenium compound which can be viewed as a starting unit.[6] In this work, we present the use of this unit to make the dinuclear ruthenium compound $[\{[Ru(bpy)(tpy)]_2(\mu\text{-dcpeb})\}(BPh_4)_2]\cdot 4(PhCH_3)$ (dcpeb = dicyanamidobiphenylethynylbenzene; Scheme 1).

Very few examples of dinuclear ruthenium complexes with long conjugated bridges are known in the literature, and even rarer are those whose X-ray structures have been solved.[5,7−9] We present here the X-ray structure of the first such dinuclear ruthenium complex with a long conjugated bridge, the through-space internuclear distance reaching 24.9 Å.



Scheme 1

Results and Discussion

The dinuclear compound was obtained by a Sonogashira cross-coupling reaction[10] adapted to the iodoruthenium complex. The use of the iodo complex was justified by its high reactivity in this kind of coupling (yield: 89%).[11]

The complex crystallises in the $P2_1/c$ space group (for crystallographic data see Table 1). The asymmetric unit consists of half a molecule of **2**, the central phenyl group lying on the inversion center. The tetraphenylborate anions are found near the angle of the bent phenylcyanamido unit, and toluene molecules fill the remaining voids of the structure.

The general shape of the molecule is a dumb-bell (see Figure 1). Interestingly, there are few reports of crystal structures containing such molecular shapes. Thus Crutchley has described the crystal structures of dinuclear complexes with dicyanamidobenzene as a bridging ligand and either $[Ru(NH_3)_5]^{3+}$,[5] *trans*-$[Ru(NH_3)_4(py)]^{3+}$ [12] or *mer*-$[Ru(NH_3)_3(bpy)]^{3+}$ [13] as terminal units (metal−metal distances 13.1, 10.9, and 13.1 Å, respectively). More recently, he has also reported the structure of [Ru(bpy)(tpy)-μ(adcp)-

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Table 1. Crystal and experimental data

Formula	$C_{150}H_{122}B_2N_{14}Ru_2$
Crystal system	Monoclinic
M(g mol^{-1})	2344.38
Space group	$P2_1/c$
a, Å	12.6957(3)
b, Å	34.0958(10)
c, Å	15.3541(4)
β	110.738(2)
V, Å^3	6215.7(3)
Z	2
λ (Mo-K_α), Å	0.71074
Calculated ρ, g cm^{-3}	1.253
2θ max, °	56
No of reflections used	26985
R_{int}	0.037
No of unique reflections	9732
No of unique reflections with $I > 3\sigma(I)$	6468
Number of variables	631
Shape	Near spherical
Absorption correction	Radius 0.1
R_{int} after correction	0.035
T min/max	0.956/0.956
$R_f = \Sigma\|\|F_0\| - \|F_c\|\|/\Sigma\|F_0\|$	0.063
$R_w = [\Sigma w(\|F_0\| - \|F_c\|)^2/\Sigma\|F_0\|^2]^{1/2}$	0.068
Agreement factor	1.648

Ru(bpy)(tpy)]·$(PF_6)_2$·DMF, where adpc is the 4,4′azodi(phenylcyanamido) dianion (metal−metal distance 19.5 Å).[9] The present molecule is longer still, with a Ru−Ru distance of 24.9 Å.

The scarcity of crystal structures with dumb-bell molecules is probably due to the fact that it is impossible to densely pack molecules made up of bulky ends connected by a thinner spacer.[14] This is why our strategy was to attempt crystallisation in the presence of a large counterion (tetraphenylborate) and also of a large solvent (toluene). Our expectation was that the large counterion and solvent molecules could fill the voids and thus stabilise the crystal structure, as already observed by Jetti et al. in the case of the dimer of 4-(triphenylmethyl)benzoic acid in the presence of either xylene or chlorobenzene.[14]

The ruthenium moiety [Ru(bpy)(tpy)(cyanamido)] is at first sight similar to the mononuclear compound described elsewhere,[6] with the NCN group in the plane of the phenylene group to which it is linked (see Figure 2). This geometry ensures a good conjugation of their π systems. The bipyridine and terpyridine planes are perpendicular, with the bipyridine plane bisecting the terpyridine. The phenylcyanamido moiety makes a dihedral angle of 79° with the bipyridine plane (see Figure 2), while this value is 28° for the mononuclear compound[6] and 58° for [Ru(bpy)(tpy)-μ(adcp)-Ru(bpy)(tpy)]$^{2+}$.[9] Since the phenylcyanamido ligand and bipyridine are not coplanar, the Ru(bpy)(tpy)-(phenylcyanamido) group is *chiral*; the two enantiomers are present in the same molecule. In solution, on the other hand, it is likely that all possible isomers are present, although because of the length of the molecule, each of the extremities of a single molecule behaves as if it were isolated with regards to the NMR spectrum.

The Ru−N(6)−C(26) moiety is slightly bent (161.5°), suggesting that the π interaction is weaker than in Ru^{III}-cyanamide complexes, for which it is almost linear.[15] The Ru−N(6) bond is shorter (2.024 Å) than in the mononuclear compound (ca. 2.08 Å), and comparable to the one observed in the complex with adpc (2.046 Å). Concerning the cyanamido group itself, one notices a short distance between the terminal nitrogen and the central carbon [N(6)−C(26) = 1.136(7) Å], showing the preponderance of the cyanamide form [$^{-}$N−C≡N] over the carbodiimide [-N=C=N] form.

The cyanamido groups of the $(dcpeb)^{2-}$ ligand adopt a *trans* disposition, as generally observed in dinuclear bis-cyanamido complexes,[5] and free ligands (dicyd)$(AsPh_4)_2$ [16] and (dcpib)$(AsPh_4)_2$,[17] where dcpib = 4,4′-dicyanamidobiphenyl. The only exception is $[\{Ru(NH_3)_4(py)\}_2\mu\text{-}(dicyd)]^{4+}$ where the cyanamide groups are *cis*.[12] The C(33)−C(34)

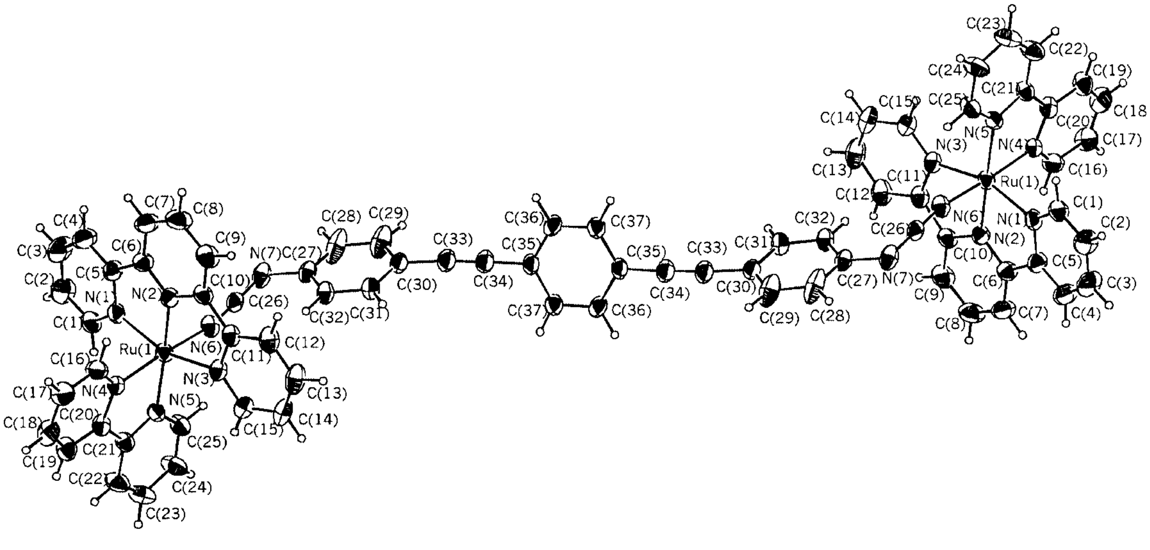

Figure 1. ORTEP drawing of the molecule of **2**

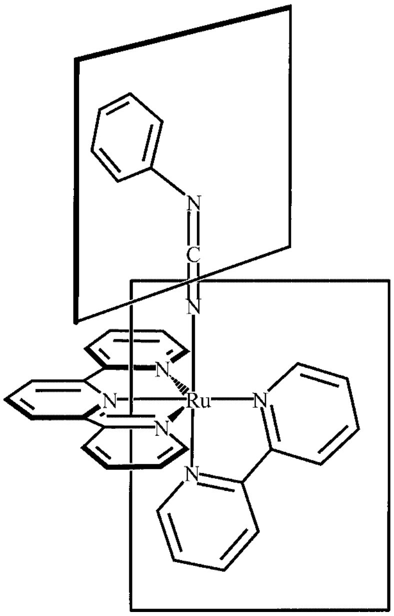

Figure 2. Coordination around ruthenium; definition of the dihedral angle between the bipyridine plane and the phenylcyanamido plane

triple bond length is 1.1863 Å, a value similar to the case of [Ru(bpy)(tpy)(pa)]$(PF_6)_2$·acetone (1.175 Å) and [Ru(bpy)(tpy)(ppa)]$(PF_6)_2$·acetone (1.187 Å) (pa = pyridylacetylene, and ppa = phenylpyridylacetylene).[18]

Of the three phenylene groups, the outer two are coplanar because of the inversion center. The dihedral angle with the central phenylene group is 65°. This value is probably not determined by intramolecular interactions, because it is known that torsion barriers around a phenylethynyl link are very small, ca. 1 kcal.[19] It is more likely determined by packing interactions. Thus, a detailed inspection of the structure shows many H···H Van der Waals contacts between the bulky Ru(bpy)(tpy) groups and tetraphenylborate and toluene molecules (H···H distances 2.60 to 2.80 Å, with an exceptionally short contact at 2.28 Å between a tpy H and a tetraphenylborate H). Consequently, the outer parts are locked in fixed positions. If free to rotate, the central phenylene group should prefer a coplanar disposition,[19] but this is prevented by a weak contact with a tetraphenylborate (H···H 2.51 Å and 2.70 Å) on one side, and with a toluene molecule on the other side.

Owing to the low torsional barrier, it is very likely that in solution there is a distribution of dihedral angles bearing on two independent torsions: between one terminal phenylene and the central one, and between the central one and the other terminal phenylene.

As far as physicochemical studies are concerned, UV/Vis spectroscopic studies of compound **1** in DMF shows two types of bands, one attributed to a $\pi \rightarrow \pi^*$ transition at 293 (94600) and 315 nm (86400 M^{-1} cm^{-1}) and the other attributed to metal-to-ligand charge-transfer bands at 397 (69800) and 493 nm (16800 M^{-1} cm^{-1}) as in similar compounds.[20,21] The cyclic voltammogram of **1** in dimethylformamide shows a quasi-reversible one-electron wave at 0.752 V vs. SCE which becomes irreversible in acetonitrile and dichloromethane. Attempts to prepare oxidized species did not lead to the appearance of any intervalence transition

Experimental Section

Physical Measurements. Electrospray (positive mode) mass spectra were obtained with a Perkin−Elmer Sciex (Nermag R10-R10) spectrometer. IR spectra were recorded as KBr pellets on a Perkin−Elmer FT-IR 1725 spectrometer. UV/Vis electronic spectra were obtained with a Shimadzu UV-3100 spectrometer. ^{1}H NMR spectra were recorded on a Bruker WF-250 spectrometer in CD_3CN solution. The solvent signal was used as internal reference at [δ_H = 1.96 ppm (CD_3CN)]. Cyclic voltammograms were obtained with an Autolab system (PGSTAT 100) (0.1 M tetrabutylammonium hexafluorophosphate, TBAH as supporting electrode) at 25 °C. A three-electrode cell was used comprising a 1 mm Pt-disk working electrode, a Pt-wire auxiliary electrode, and an aqueous saturated calomel (SCE) reference electrode.

{[Ru(bpy)(tpy)]$_2$(μ-dcpeb)}$(PF_6)_2$ (1): [Ru(bpy)(tpy)(Ipcyd)](PF_6)[6] (250 mg, 0.28 mmol) was placed in a small Schlenk tube together with [$PdCl_2(PPh_3)_2$] (4 mg, 0.007 mmol) and CuI (3 mg, 0.014 mmol). The powders were dissolved in a piperidine/DMF (1:1) mixture (3 mL) and carefully degassed under vacuum/argon several times. After stirring for 15 minutes, diethynylbenzene (18 mg, 0.14 mmol) was added to the solution. The reaction was continued all night at room temperature under argon. The solvents were then removed under vacuum and the product purified on an acidic alumina column (toluene/acetonitrile 60:40). The starting material was eliminated as a pink band, and a brown fraction of the dinuclear compound was then obtained. Recrystallisation was achieved by addition of toluene to an acetonitrile solution of **1**, which crystallised as long black needles (206 mg, 89%). IR (KBr disc): $\tilde{\nu}$ = 2160 cm^{-1} (N=C=N). ^{1}H NMR (250 MHz, CD_3CN, 20 °C, TMS): δ = 9.76 (d, *J* = 5.7 Hz, 2 H, H-a), 8.62 (d, *J* = 8.1 Hz, 2 H, H-d), 8.53 (d, *J* = 8.1 Hz, 4 H, H-3′), 8.42 (d, *J* = 8.1 Hz, 4 H, H-3), 8.32 (d, *J* = 7.9 Hz, 2 H, H-e), 8.28 (td, *J* = 8.1, 7.7 Hz, 2 H, H-c), 8.17 (t, *J* = 7.7, 8.5 Hz, 2 H, H-4′), 7.95 (t, *J* = 7.7, 8.1 Hz, 4 H, H-4), 7.95(m, 2 H, H-b), 7.73 (m, 6 H, H_{6+f}), 7.39 (s, 4 H), 7.37 (dq, *J* = 6.5 Hz, 2 H, H-h), 7.32 (dd, *J* = 5.5, 7.7 Hz, 4 H, H-5), 7.21 (d, *J* = 7.3 Hz, 2 H, H-g), 7.02 (d, *J* = 8.7 Hz, 4 H, H-m,m′), 6.07 (d, *J* = 8.7 Hz, 4 H, H-o,o′). (see Scheme 1 for atom numbering). MS (ES) for $C_{74}H_{50}F_6N_{14}PRu_2$ [M − PF_6]$^+$: *m*/*z*: calcd. 1483.2; found 1483.3; for [M − 2PF_6]$^{2+}$/2: calcd. 669.3; found 669.1; for [M − 2PF_6 − [Ru(bpy)(tpy)] + H$^+$]$^+$: calcd. 848.2; found 848.2. $C_{74}H_{50}F_{12}N_{14}P_2Ru_2(Al_2O_3)$ (1730.1): calcd. C 51.3, H 2.9, N 11.3; found C 51.4, H 2.8, N 11.0.

{[Ru(bpy)(tpy)]$_2$(μ-dcpeb)}$(BPh_4)_2$.4(Ph-CH_3) (2): Compound **1** was dissolved in acetonitrile. Subsequent addition of tetrabutylammonium bromide (in excess) precipitated the bromide salt of the complex, which was filtered and rinsed with ether. Dissolution of the bromide salt in methanol/water (1:1 mixture), followed by addition of sodium tetraphenylborate (excess) precipitated [{Ru(bpy)(tpy)]$_2$(μ-dcpeb)}]$(BPh_4)_2$. Slow diffusion of toluene into an acetonitrile solution of [{Ru(bpy)(tpy)]$_2$(μ-dcpeb)}]$(BPh_4)_2$ led to the desired complex **2**.

X-ray Crystallographic Study: Recrystallisation was performed by slow diffusion of toluene into an acetonitrile solution of the tetraphenylborate salt of the complex. Brown needles were obtained. A single crystal was chosen to perform the X-ray diffraction measurements. Reflection data for the crystal were measured using a Nonius Kappa CCD diffractometer at room temperature, using graphite monochromated Mo-K_α radiation ($\lambda = 0.71074$ Å) at a detector distance of 4 cm and a swing angle of 20° (this type of crystal, being unfortunately very small, and showing poor quality of crystallinity, did not give observable spots at wider angles). To increase the quality of the collected data, we tried to perform measurements at low temperature, but the crystal broke due to the very poor mosaicity found at room temperature. The crystallographic cell was found by using HKL Scalepack.[22] The structure was solved using SIR92[23] and refined in the Maxus software package.[24]

The asymmetric unit contains a tetraphenylborate counteranion, and two toluene solvent molecules. The refinement was performed anisotropically for all the non-hydrogen atoms of the complex. The hydrogen atoms were localized by difference Fourier synthesis, recalculated and fixed at 0.96 Å, then their contributions were introduced in the calculations but not refined. For the toluene atoms, due to their high thermal vibration, they were refined in isotropic positions; nevertheless it was difficult to position them, so for the last refinement, they were left fixed at their last atomic positions in order not to disturb the overall geometry of the complex. 6468 reflections [$I > 3\sigma(I)$] were used for the 631 parameters and the R value dropped to 0.0634.

CCDC-179708 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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