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Ruthenium bipyridine complexes: synthesis and characterisation of $Ru(tmbpy)(CO)_2Cl_2$, $Ru(dmbpy)(CO)_2Cl_2$ and $[Ru(dmbpy)(CO)_2Cl]_2$

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Abstract

Ruthenium carbonyl complexes with methyl substituted 2,2′-bipyridine ligands have been synthesised. $[Ru(CO)_3Cl_2]_2$ reacts with 4,4′,5,5′-tetramethyl 2,2′-bipyridine (tmbpy) and 4,4′-dimethyl 2,2′-bipyridine (dmbpy) in THF to form mononuclear *cis*-CO, *cis*-Cl complexes, whereas in ethylene glycol/octanol solution the product with dmbpy is dimeric. The dimeric complex $[Ru(bpy)(CO)_2Cl]_2$ has been re-measured and refined in space group $P2/c$. The complexes have been characterised by spectroscopic studies and X-ray diffraction measurements: $Ru(tmbpy)(CO)_2(Cl)_2$ (**1**), orthorhombic, space group $P2_12_12_1$, $a = 9.372(2)$ Å, $b = 12.779(1)$ Å, $c = 15.320(3)$ Å, $Z = 4$; $Ru(dmbpy)(CO)_2(Cl)_2$ (**2**), monoclinic, space group $P2_1/c$, $a = 11.754(4)$ Å, $b = 12.920(3)$ Å, $c = 14.245(3)$ Å, $\beta = 111.74(2)°$ $Z = 4$; $[Ru(dmbpy)(CO)_2Cl]_2$ (**3**), monoclinic, space group $C2/c$, $a = 21.485(7)$ Å, $b = 11.900(4)$ Å, $c = 14.924(3)$ Å, $\beta = 130.30(3)°$, $Z = 4$.

Keywords: Ruthenium; Carbonyls; Bipyridine

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1. Introduction

Over the past few years, Ru(II)polypyridine complexes have been widely studied because of their activity in various catalytic processes [1–6]. Recently, there has been a growing interest in synthesising new Ru(II) complexes in order to determine the reactivity of these compounds in ligand substitution reactions and in the characterisation of the resulting products [7–9]. Some of these complexes can be seen as possible intermediates in different catalytic cycles thus giving new information about the mechanisms of these processes [9]. Substituted bipyridine ligands have been used to change the electronic and steric properties of Ru-complexes [10–13], which can be seen to affect the coordination of other ligands to the metal centre. From the catalysis point of view the monomeric ruthenium bipyridines have proved to be effective precursors for highly active water gas shift and CO_2 reduction catalysts. A polymeric structure with direct Ru–Ru bonds has been proposed for the active species. However, the detailed structural characterization of the polymer has not been successful so far. The synthesis and characterisation of monomeric and dimeric precursors is the prerequisite for the understanding of the activity of the catalyst.

In this work, we report the synthesis and spectroscopic properties of the new methyl substituted bipyridine–ruthenium complexes $Ru(tmbpy)(CO)_2Cl_2$ (**1**), (tmbpy = 4,4′,5,5′-tetramethyl 2,2′-bipyridine), $Ru(dmbpy)(CO)_2Cl_2$ (**2**), and $[Ru(dmbpy)(CO)_2Cl]_2$ (**3**) (dmbpy = 4,4′-dimethyl 2,2′-bipyridine) and report the structural characterisation of these Ru–polypyridine complexes. Furthermore, we have measured and re-refined the dimeric complex $[Ru(bpy)(CO)_2Cl]_2$ (**4**) in space group $P2/c$.

2. Experimental

2.1. Materials

$[Ru(CO)_3Cl_2]_2$ was purchased from Johnson & Matthey and 4,4′-dimethyl bipyridine from Aldrich

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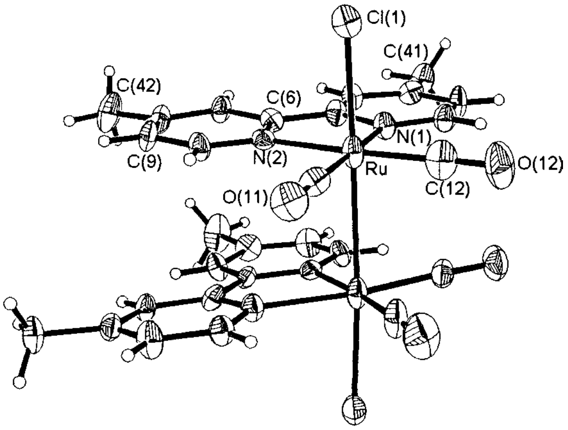

Fig. 1. The structure of [Ru(dmbpy)$(CO)_2$Cl] (**3**).

Chemicals. The preparation of 4,4′,5,5′-tetramethyl bipyridine followed the method described by Sasse and Whittle [14–17]. The product, a colourless crystalline solid, mp 257–257.5°C, was characterised by microanalysis, ^{1}H and ^{13}C NMR, and mass spectrometry [14–17]. All solvents used were analytical grade and they were used as received. The syntheses of Ru(tmbpy)$(CO)_2Cl_2$, Ru(dmbpy)$(CO)_2Cl_2$, and $[Ru(dmbpy)(CO)_2Cl]_2$ were performed air-sensitively with traditional vacuum-line techniques. All manipulations of the products were performed in air.

2.2. Spectroscopic studies

Infrared spectra were measured with a Nicolet Magna 750 FTIR spectrometer from CH_2Cl_2 solutions or from KBr discs. ^{1}H and ^{13}C NMR spectra were recorded by using Bruker AMX 400 spectrometer and $CDCl_3$ as a solvent.

*2.3. Synthesis of Ru(tmbpy)$(CO)_2Cl_2$ (**1**), tmbpy = 4,4′,5,5′-tetramethyl 2,2′-bipyridine*

$[Ru(CO)_3Cl_2]_2$ (292 mg, 0.57 mmol) and tmbpy (242 mg, 1.14 mmol) were separately dissolved in 20 ml portions of THF under nitrogen. $[Ru(CO)_3Cl_2]_2$ and tmbpy solutions were combined and the mixture was refluxed continuously under nitrogen for 30 min. During this time, a colour change in the mixture from light

Table 1
Crystallographic data for Ru(tmbpy)$(CO)_2(Cl)_2$ (**1**), Ru(dmbpy)$(CO)_2Cl_2 \cdot CDCl_3$ (**2**), $[Ru(dmbpy)(CO)_2Cl]_2$ (**3**), and $[Ru(bpy)(CO)_2Cl]_2$ (**4**) (tmbpy = 4,4′,5,5′-tetramethyl 2,2′-bipyridine, dmbpy = 4.4′-dimethyl 2,2′-bipyridine)

	1	**2**	**3**	**4**
Fw	440.28	531.59	753.55	697.45
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	$P2_12_12_1$	$P2_1/c$	$C2/c$	$P2/c$
a, Å	9.372(2)	11.754(4)	21.485(7)	10.572(2)
b, Å	12.779(1)	12.920(3)	11.900(4)	10.117(2)
c, Å	15.320(3)	14.245(3)	14.924(3)	12.619(2)
α, deg.	90	90	90	90
β, deg.	90	111.74(2)	130.30(3)	114.02(2)
γ, deg.	90	90	90	90
V, Å^3	1834.8(6)	2009.4(9)	2910(2)	1232.8(4)
Z	4	4	4	2
D_{calc}, g/cm^3	1.594	1.757	1.720	1.879
Crystal source	acetone/methanol	$CDCl_3$	glycol/1-octanol	glycol
Crystal size, mm	0.3 × 0.5 × 0.8	0.1 × 0.2 × 0.2	0.1 × 0.1 × 0.2	0.1 × 0.1 × 0.2
Color	yellow	yellow	red	red
Radiation	MoKα	MoKα	MoKα	MoKα
μ, mm^{-1}	1.15	1.46	1.26	1.48
2θ limits, deg.	5–60	5–50	5–50	5–55
h range	0–13	0–13	0–25	0–13
k range	0–17	0–15	0–14	0–13
l range	0–21	−16 to 15	−17 to 13	−16 to 14
No. of unique reflections	2985	3526	2544	2838
No. of observed data[a]	2564	1497	990	1532
No. of params	209	229	181	163
$R1$ (F_o)	0.0500	0.0467	0.0483	0.0560
$wR2$ (F_o^2)[b]	0.1214	0.0948	0.1193	0.1546
x	0.0530	0.0286	0.0464	0.0883
y	2.50	0.00	0.00	0.00
Goodness of fit	1.100	0.729	0.732	0.841

[a] $I \geq 2\sigma(I)$.
[b] $w = 1[\sigma^2(F_o^2) + (xP)^2 + yP]$, $P = (F_o^2 + 2F_c^2)/3$.

Table 2
Selected bond lengths (Å) for $Ru(tmbpy)(CO)_2(Cl)_2$ (**1**), $Ru(dmbpy)(CO)_2Cl_2 \cdot CDCl_3$ (**2**), $[Ru(dmbpy)(CO)_2Cl]_2$ (**3**), and $[Ru(bpy)(CO)_2Cl]_2$ (**4**) in $P2/c$ (tmbpy = 4,4′,5,5′-tetramethyl 2,2′-bipyridine, dmbpy = 4.4′-dimethyl 2,2′-bipyridine)

	1	**2**	**3**	**4**
Ru(1)–Cl(1)	2.422(2)	2.426(2)	2.509(3)	2.497(2)
Ru(1)–Cl(2)	2.393(2)	2.393(2)		
Ru(1)–N(1)	2.107(5)	2.095(6)	2.129(7)	2.126(7)
Ru(1)–N(2)	2.070(5)	2.049(6)	2.112(7)	2.122(6)
Ru(1)–C(11)	1.883(7)	1.899(8)	1.837(10)	1.826(8)
Ru(1)–C(13)[a]	1.889(8)	1.852(9)	1.847(12)	1.862(9)
C(11)–O(11)	1.133(8)	1.108(8)	1.140(10)	1.169(10)
C(13)–O(13)[a]	1.101(9)	1.127(8)	1.155(11)	1.163(10)
C(2)–C(51)	1.524(10)			
C(3)–C(41)	1.505(11)	1.479(9)	1.507(11)	
C(8)–C(42)	1.516(11)	1.510(9)	1.522(12)	
C(9)–C(52)	1.495(9)			
Ru–Ru			2.854(2)	2.848(1)

[a] C(13) = C(12) for **3** and **4**, O(13) = O(12) for **3**.

yellow to nearly orange was observed. After 30 min of refluxing a light yellow precipitate was formed, which was separated by filtration and air-dried after the cooling of the reaction mixture. The recrystallisation of the precipitate (0.325 g, 65%) from an acetone–methanol solution yielded light yellow crystals suitable for X-ray diffraction measurement. (Found: C, 43.6; N, 6.4; H, 3.65. $C_{16}H_{16}Cl_2N_2O_2Ru$ requires: C, 43.65; N, 6.4; H, 3.7). ν_{max}/cm^{-1} (CO) 2065 (vs), 2000 (vs) (CH_2Cl_2). $^{13}C\{^1H\}$ NMR for aromatic rings in tmbpy ($CDCl_3$): ten peaks δ 155.5–123.8; for CO: δ 195.9 (s), 191.4 (s), for Me: δ 20.4 (s), 17.5 (s). ^1H NMR for aromatic protons in tmbpy: δ 9.4 (s), 8.5 (s).

Table 3
Selected bond angles (deg.) for $Ru(tmbpy)(CO)_2(Cl)_2$ (**1**), $Ru(dmbpy)(CO)_2Cl_2 \cdot CDCl_3$ (**2**), $[Ru(dmbpy)(CO)_2Cl]_2$ (**3**), and $[Ru(bpy)(CO)_2Cl]_2$ (**4**) in $P2/c$ (tmbpy = 4,4′,5,5′-tetramethyl 2,2′-bipyridine, dmbpy = 4.4′-dimethyl 2,2′-bipyridine)

	1	**2**	**3**	**4**
Cl(1)–Ru(1)–C(13)[a]	178.7(2)	178.0(3)	176.8(1)	175.8(1)
Cl(1)–Ru(1)–N(1)	86.9(2)	86.1(2)	85.3(2)	85.0(2)
Cl(1)–Ru(1)–N(2)	87.2(2)	86.6(2)	85.6(2)	83.8(2)
Cl(1)–Ru(1)–C(11)	89.6(2)	89.5(2)	97.8(3)	94.7(3)
Cl(1)–Ru(1)–Cl(2)[b]	89.2(1)	90.6(1)	93.2(4)	97.3(3)
N(1)–Ru(1)–N(2)	78.2(2)	78.2(2)	76.8(3)	76.3(3)
N(1)–Ru(1)–Cl(2)[b]	93.8(2)	95.0(2)	98.6(4)	98.3(4)
N(2)–Ru(1)–C(11)	99.1(3)	98.3(3)	98.0(4)	100.5(3)
C(11)–Ru(1)–Cl(2)[b]	88.8(2)	88.3(2)	86.7(4)	84.9(4)
N(1)–Ru(1)–C(11)	175.6(3)	174.6(3)	173.8(4)	176.8(3)
N(2)–Ru(1)–Cl(2)[b]	171.3(2)	172.8(2)	175.3(4)	174.4(3)
C(1)–C(2)–C(51)	120.0(8)			
C(2)–C(3)–C(41)	121.8(8)	123.9(8)	122.5(9)	
C(7)–C(8)–C(42)	119.9(8)	121.4(8)	120.7(9)	
C(8)–C(9)–C(52)	122.6(7)			

[a] C(13) = Ru for **3** and **4**.
[b] Cl(2) = C(12) for **3** and **4**.

*2.4. Synthesis of $Ru(dmbpy)(CO)_2Cl_2$ (**2**), dmbpy = 4,4′-dimethyl 2,2′-bipyridine*

$Ru(dmbpy)(CO)_2Cl_2$ was synthesised from $[Ru(CO)_3Cl_2]_2$ and 4,4′-dimethyl 2,2′-bipyridine by refluxing in THF in the same manner as in case **1**, except that the molar ratio Ru: dmbpy was 1:2 ($[Ru(CO)_3Cl_2]_2$ weighted 0.250 g, 0.5 mmol). The light yellow precipitate formed during the refluxing was collected after cooling the reaction mixture and dried in air. The resulting complex (0.288 g, 72%) was characterised by spectroscopic methods, elemental analysis, and X-ray diffraction analysis (crystals obtained from $CHCl_3$ as solvated $Ru(dmbpy)(CO)_2Cl_2$ $CHCl_3$). (Found: C, 40.9; N, 6.6; H, 2.9. $C_{14}H_{12}Cl_2N_2O_2Ru$ requires C, 40.8; N, 6.8; H, 2.9). ν_{max}/cm^{-1} (CO) 2063 (vs), 1999 (vs) (CH_2Cl_2). $^{13}C\{^1H\}$ NMR for aromatic rings in dmbpy ($CDCl_3$): ten peaks δ 155.4–124.1; for CO: δ 195.5 (s), 190.9 (s); for Me: δ 22.4 (s), 22.2 (s). ^1H NMR for Me: δ 2.61 (s), 2.57 (s). The mono(bipyridine) complex **2** was the only product detected despite the excess of the bipyridine ligand.

*2.5. Synthesis of $[Ru(dmbpy)(CO)_2Cl]_2$ (**3**), dmbpy = 4,4′-dimethyl 2,2′-bipyridine*

$[Ru(CO)_3Cl_2]_2$ (1.0 g, 2.0 mmol) was introduced into 5 ml of ethylene glycol and the mixture gently heated under nitrogen. The resulting yellow solution was added

Table 4
Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$Å^2 \times 10^3$] for $Ru(tmbpy)(CO)_2(Cl)_2$ (**1**)

Atom	x	y	z	U_{eq}
Ru(1)	9618(1)	861(1)	9893(1)	38(1)
Cl(1)	7143(2)	911(2)	9440(1)	56(1)
Cl(2)	10161(2)	−163(2)	8628(1)	60(1)
C(11)	9973(8)	2077(6)	9234(5)	48(2)
O(11)	10168(7)	2807(5)	8831(4)	72(2)
C(13)	11542(8)	791(6)	10258(5)	51(2)
O(13)	12681(7)	732(6)	10425(5)	89(2)
N(1)	9069(7)	−451(4)	10656(3)	42(1)
N(2)	8966(6)	1554(4)	11047(3)	38(1)
C(1)	9259(10)	−1460(5)	10452(5)	53(2)
C(2)	8856(11)	−2275(6)	10975(5)	56(2)
C(3)	8184(10)	−2054(5)	11771(5)	55(2)
C(4)	7954(10)	−1010(5)	11984(5)	51(2)
C(5)	8420(8)	−219(5)	11426(4)	41(1)
C(6)	8364(7)	906(5)	11642(4)	40(1)
C(7)	7793(9)	1302(6)	12412(5)	50(2)
C(8)	7819(9)	2365(6)	12582(5)	51(2)
C(9)	8486(8)	3026(5)	11983(5)	44(2)
C(10)	9018(8)	2580(5)	11231(4)	43(1)
C(41)	7757(14)	−2908(7)	12395(6)	76(3)
C(42)	7141(12)	2786(7)	13409(6)	76(3)
C(51)	9138(14)	−3398(6)	10689(6)	80(3)
C(52)	8614(9)	4180(5)	12122(5)	55(2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 5
Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{Å}^2 \times 10^3$] for Ru(dmbpy)(CO)$_2$(Cl)$_2 \cdot$CDCl$_3$ (**2**)

Atom	x	y	z	U_{eq}
Ru	3283(1)	1851(1)	5642(1)	44(1)
Cl(1)	1422(2)	2560(2)	5746(2)	60(1)
Cl(2)	3438(2)	3293(2)	4642(2)	64(1)
C(11)	4218(7)	2616(6)	6812(6)	48(2)
O(11)	4738(6)	3019(5)	7530(5)	93(2)
C(31)	4685(8)	1324(7)	5516(6)	56(2)
O(31)	5563(6)	1062(5)	5443(5)	88(2)
N(1)	2129(5)	987(5)	4414(4)	41(2)
N(2)	2959(5)	564(4)	6346(5)	42(2)
C(1)	1741(7)	1240(6)	3437(6)	48(2)
C(2)	889(8)	663(7)	2702(6)	54(2)
C(3)	404(7)	−215(7)	2914(6)	48(2)
C(4)	823(7)	−497(6)	3935(6)	48(2)
C(5)	1688(6)	100(6)	4666(5)	38(2)
C(6)	2164(6)	−147(6)	5764(5)	37(2)
C(7)	1817(7)	−1003(6)	6138(6)	45(2)
C(8)	2321(8)	−1197(6)	7176(6)	50(2)
C(9)	3153(8)	−483(7)	7767(6)	60(2)
C(10)	3454(7)	365(6)	7347(6)	51(2)
C(41)	−515(7)	−858(7)	2142(6)	66(3)
C(42)	1944(8)	−2129(5)	7632(6)	74(3)
Cl(3)	3771(2)	8788(2)	472(2)	103(1)
Cl(4)	1251(2)	8960(2)	266(2)	94(1)
Cl(5)	3203(2)	9669(2)	2073(2)	89(1)
C(51)	2688(9)	9522(7)	738(7)	68(3)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

to a mixture of dmbpy (1.1 g, 9.4 mmol), ethylene glycol (10 ml) and 1-octanol (10 ml) by syringe. The reaction mixture was first heated at 75°C for 7 h, allowed to stand several days under nitrogen at 65°C, and then the reaction mixture was cooled to room temperature. The red microcrystalline precipitate (1.016 g, 68%) was filtered, washed with small amounts of methanol and dried in air. A crystal suitable for X-ray diffraction measurement was obtained from the precipitate without recrystallisation. (Found: C, 44.9; N, 7.5; H, 3.3. $C_{28}H_{24}Cl_2N_4O_4Ru_2$ requires C, 44.6; N, 7.4; H, 3.2). ν_{max}/cm^{-1} (CO) 2020 (br, vs), 1977 (s), 1928 (br, vs) (KBr). Poor solubility of the dimeric complex prevented NMR-studies (Fig. 1).

Table 6
Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{Å}^2 \times 10^3$] for [Ru(dmbpy)(CO)$_2$Cl]$_2$ (**3**)

Atom	x	y	z	U_{eq}
Ru	4659(1)	2212(1)	3062(1)	45(1)
Cl(1)	4087(1)	2323(2)	4087(2)	55(1)
N(1)	5684(4)	3077(6)	4557(6)	43(2)
N(2)	4321(4)	3919(6)	2637(6)	37(2)
C(11)	3761(6)	1595(8)	1677(9)	49(3)
O(11)	3203(4)	1196(6)	832(6)	72(2)
C(12)	5026(6)	757(10)	3558(9)	65(3)
O(12)	5263(5)	−149(6)	3878(7)	92(3)
C(1)	6354(5)	2615(8)	5525(7)	46(2)
C(2)	6992(5)	3222(8)	6464(8)	56(3)
C(3)	6950(5)	4369(8)	6460(8)	45(2)
C(4)	6240(5)	4852(7)	5491(7)	42(2)
C(5)	5604(6)	4220(8)	4530(8)	42(3)
C(6)	4861(5)	4690(8)	3481(8)	38(2)
C(7)	4678(6)	5832(7)	3303(7)	44(3)
C(8)	3979(6)	6223(8)	2270(8)	52(3)
C(9)	3432(6)	5445(8)	1452(8)	53(3)
C(10)	3605(5)	4310(8)	1637(7)	45(3)
C(41)	7637(5)	5082(8)	7457(8)	58(3)
C(42)	3816(6)	7479(7)	2052(10)	83(4)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 7
Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{Å}^2 \times 10^3$] for [Ru(bpy)(CO)$_2$Cl]$_2$ (in $P2/c$) (**4**)

Atom	x	y	z	U_{eq}
Ru	3673(1)	7582(1)	1555(1)	31(1)
Cl(1)	1292(2)	7462(2)	−22(2)	45(1)
N(1)	2650(7)	8060(7)	2647(6)	43(2)
N(2)	3161(7)	5711(6)	2031(6)	43(2)
C(11)	4540(9)	7075(9)	630(7)	47(2)
O(11)	5015(8)	6686(8)	0(6)	75(2)
C(12)	4085(9)	9294(9)	1254(7)	51(2)
O(12)	4342(8)	10378(6)	1106(6)	77(2)
C(1)	2375(9)	9316(8)	2903(8)	45(2)
C(2)	1703(11)	9585(11)	3573(9)	70(3)
C(3)	1190(10)	8524(11)	4011(8)	60(3)
C(4)	1418(8)	7267(10)	3746(7)	52(2)
C(5)	2138(8)	7079(8)	3015(7)	41(2)
C(6)	2434(9)	5731(8)	2700(7)	40(2)
C(7)	1882(10)	4595(8)	2940(8)	57(2)
C(9)	2856(12)	3370(10)	1830(9)	71(3)
C(8)	2122(13)	3405(11)	2518(9)	79(3)
C(10)	3426(10)	4573(8)	1612(8)	59(3)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

2.6. X-ray data collection and structure solutions

X-ray diffraction data were collected with a Nicolet R3m diffractometer (complex **1**) or a Syntex P21 (complexes **2** and **3**) using graphite monochromated MoKα radiation ($\lambda = 0.71073$ Å). The crystals suitable for X-ray diffraction studies were carefully chosen by microscopic examination and mounted on glass fibers. Cell parameters were obtained from 25 automatically centred reflections. Intensities were corrected for background, polarization and Lorentz factors. Data collection, data reduction and cell refinement were carried out with the P3/P4-diffractometer program V 4.27 [18–20]. The structures were solved by direct methods. The structure solution was carried out with the SHELXS 86 program and structure refinement with the SHELXL 93 program [18–20]. All non-hydrogen atoms were refined anisotropically. Aromatic hydrogens and methyl group hydrogens were placed in idealised positions (aromatic

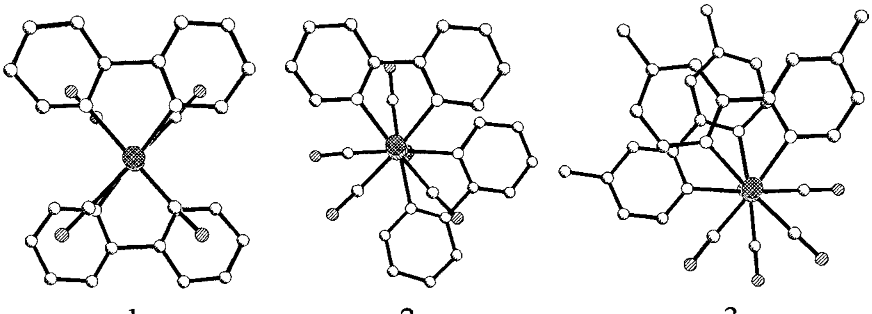

Fig. 2. Topside view of the dimeric complexes $[Ru(bpy)(CO)_2Cl]_2$ (**1**) in $C2/m$, $[Ru(bpy)(CO)_2Cl]_2$ (**2**) in both $C2/m$ and $P2/c$, and $[Ru(dmbpy)(CO)_2Cl]_2$ (**3**).

C–H = 0.93 Å, methyl C–H = 0.96 Å). Chloroform hydrogen in **2** was located from the difference Fourier map and refined isotropically with fixed isotropic displacement parameter ($U = 0.05$ Å^2). No decomposition of the complexes studied was observed during the data collection with the X-ray diffractometer. The crystallographic data are collected in Table 1, the selected bond lengths, bond angles, and refined atomic coordinates in Tables 2–7.

The unit cells of $[Ru(bpy)(CO)_2Cl]_2$ were determined for twelve different crystals from several separate synthesis. Two crystals belong unambiguously to space group $P2/c$ while 10 crystals belong to space group $C2/m$. The structure solution in $C2/m$ has been reported earlier [9], including disordered mixture of two rotamers: staggered and 'anti eclipsed' (Fig. 2). Structure solution in space group $P2/c$ gave a staggered rotamer without disorder. These results show that the dimer crystallizes in two different space groups and the ratio of two isomers varies from crystal to crystal. Since the structural solution in $C2/m$ is the same as the solution reported earlier [9], it has been added here only as a supplementary material. [1]

3. Results and discussion

Different substituent groups attached to bipyridine rings can be seen to be simple tools for modifying the properties of Ru–bipyridine complexes. The substituent groups, either electron withdrawing or electron pushing, can alter the electronic properties of these complexes, which can be detected, for example, by cyclic voltammetry and by spectral studies [10,11,21]. Sterically hindering groups attached to 2,2′-bipyridine rings may alter the coordination properties of the metal centre in Ru–bpy complexes, depending on the position of the substituent groups in the bpy ligand [12,13]. In addition, methyl substitution of 2,2′-bipyridine has been reported to enhance the solubility of resulting complexes in common organic solvents [12].

For both the methyl substituted Ru-monomers synthesised in this work, only a very slight low-frequency shift of the CO stretching bands was observed in comparison to the unsubstituted Ru-complex $Ru(bpy)(CO)_2Cl_2$ (ν(CO) in dichloromethane: 2065 cm^{-1} and 2000 cm^{-1} for $Ru(tmbpy)(CO)_2Cl_2$ (**1**), 2063 cm^{-1} and 1999 cm^{-1} for $Ru(dmbpy)(CO)_2Cl_2$ (**2**) vs. 2067 cm^{-1} and 2003 cm^{-1} for $Ru(bpy)(CO)_2Cl_2$ [9]). It may be noted here that the changes in carbonyl stretching frequencies with complexes concerned in this paper require changes in the electron density of the metal centre, due to differently substituted polypyridine ligands, which in turn has been reported to be dependent on the distortions of the bipyridine rings [22]. For both monomeric complexes, slight distortions of the methyl substituted bipyridine rings was observed (see below). No changes in the ν(CO) bands could be reliably detected for the methyl substituted Ru dimer $[Ru(dmbpy)(CO)_2Cl]_2$ owing to the poor solubility of both this complex and the corresponding unsubstituted dimer $[Ru(bpy)(CO)_2Cl]_2$ [9] (the IR spectra for these compounds were measured as KBr discs, which tend to broaden the stretching bands observed). A much more significant high-frequency shift of the CO stretching bands is observed when the Cl-ligands are replaced by SCN-groups [13] (ν(CO) in dichloromethane: 2071 (s) and 2020 cm^{-1} for $Ru(bpy)(CO)_2(SCN)_2$), which indicates a somewhat decreased electron density in the metal centre of this complex.

The reactions of $[Ru(CO)_3Cl_2]_2$ with both tmbpy and dmbpy in THF are essentially similar; in both cases the products are octahedral ruthenium bipyridine complexes, as verified by single crystal X-ray crystallography. Although the crystal structures of the free ligands tmbpy and dmbpy have not been determined, the structural effects of the coordination of related substituted

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[1] Selected bond lengths for $[Ru(bpy)(CO)_2Cl]_2$ in $C2/m$: Ru–Ru 2.847(1) Å, Ru–Cl 2.498(2) Å, Ru–N 2.038(6) and 2.156(6) Å, Ru–C 1.816(7) and 1.953(9) Å. Complete structural data are available as supporting information.

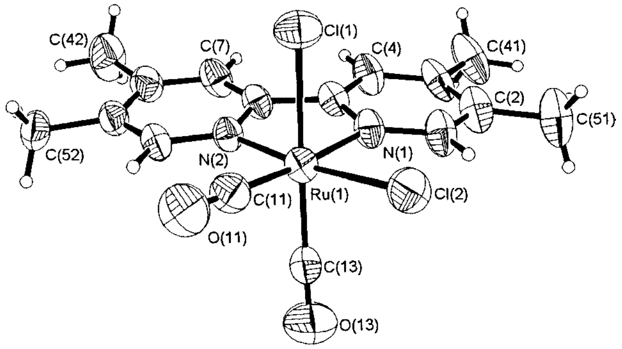

Fig. 3. The structure of Ru(dmbpy)$(CO)_2(Cl)_2 \cdot CDCl_3$ (**2**). The solvent molecule has been omitted for clarity.

bipyridine ligands to a metal tetracarbonyl centre have previously been studied crystallographically [14–17,22]. The structures for complexes **1** and **2** are given in Figs. 3 and 4. The substituent methyl groups in 4,4′,5,5′- or 4,4′ positions in bpy rings do not interfere with the coordination of these polypyridine ligands to the metal centre, which is clearly shown in the nearly planar arrangement of the bpy ring halves in these compounds. The dihedral angle between the planes of the bipyridine ring halves is about 1.6° for Ru(dmbpy)$(CO)_2Cl_2$ and 8.1° for Ru(tmbpy)$(CO)_2Cl_2$, with the aromatic ring normals being slightly bent away from the axial carbonyls. As a comparison, the corresponding value for 6,6′-dimethyl substituted Ru–dmbpy analogue is 16° [13], which indicates considerable strain in the bipyridine ring system of this complex, mainly due to the electronic repulsion of the methyl groups and the carbonyl ligands in the equatorial plane in this complex.

The bipyridine ring halves are not chemically equivalent for either of the mononuclear Ru–bpy complexes studied, as indicated by the 10-peak patterns in the aromatic region of the ^{13}C NMR spectra of complexes **1** and **2**. Similarly, the two carbonyl resonances found for both of these complexes indicated that different ligands are positioned *trans* to the CO ligands, which confirms the *cis*-CO, *cis*-Cl structures for these complexes (in $CDCl_3$). The Ru–N bond lengths *trans* to CO ligands are slightly longer than the corresponding values *trans* to Cl ligands, which shows the trans effect of the carbonyl groups (2.107(5) Å and 2.095(6) Å vs. 2.070(5) Å and 2.049(6) Å for complexes **1** and **2**, respectively). Otherwise the observed bond lengths and angles are rather typical of the Ru-mono(2,2′-bipyridine) complexes reported earlier [9,13]. The selected bond lengths and angles for complexes studied in this work are given in Tables 2 and 3.

Since these complexes withstand rather harsh conditions, they can be seen as intriguing starting materials for further modified compounds. Methyl groups in 4,4′-dimethyl substituted bipyridine have been converted to carboxylic acid or trichlorosilylethyl groups to anchor ruthenium bipyridine compounds to TiO_2 or SnO_2 surfaces for photochemical applications [23–27]. According to our experience, the methyl groups in **2** may be converted to carboxylic acid groups in oxidising acidic solution [28].

As noted from the syntheses of the monomeric and dimeric complexes, the solvent used determined the reaction products. After filtration of the poorly soluble dimeric complex (**3**) from the glycol/octanol solution, a second precipitate was obtained from the brownish yellow alcoholic solution after prolonged standing. Similarly to the synthesis of $[Ru(bpy)(CO)_2Cl]_2$ [9], the precipitate consisted of two compounds, the ‘high-pair’ (identified as complex **2**) and the ‘low pair’ compound (ν_{max}/cm^{-1} (CO) in CH_2Cl_2: 2033, 1963), which may be identified as monomeric hydride Ru(dmbpy)$(CO)_2$ClH.

The IR spectrum of $[Ru(dmbpy)(CO)_2Cl]_2$ (**3**) is quite similar to that reported earlier for $[Ru(bpy)(CO)_2Cl]_2$ [9], indicating the formation of Ru–bpy dimer in ethylene glycol/octanol solution. The crystal structure of complex **3** was resolved by X-ray diffraction measurement with a single crystal obtained directly from the reaction mixture. The bond lengths and angles observed for $[Ru(dmbpy)(CO)_2Cl]_2$ closely resemble the corresponding values for the unsubstituted Ru–bpy dimer resolved in space group $P2/c$ (**4**), the Ru–N(bpy) bonds are almost equally long (2.129(7) and 2.112(7) Å for $[Ru(dmbpy)(CO)_2Cl]_2$ vs. 2.126(7) and 2.122(6) Å for $[Ru(bpy)(CO)_2Cl]_2$) with almost identical bipyridine ‘bite angles’ N(1)–Ru–N(2) (76.8(3)° vs. 76.3(3)°). The Ru–Ru bond distances (2.854(2) Å for **3** and 2.848(1) for **4**) are comparable with the value reported earlier for $[Ru(bpy)(CO)_2Cl]_2$ (2.860(1)) resolved in space group $C2/m$ [9]. In both cases, the axial Ru–Cl bonds are affected by the Ru–Ru-bond, resulting in relatively long Ru–Cl bond distances (2.509(3) Å for **3** and 2.497(2) for **4**).

$[Ru(dmbpy)(CO)_2Cl]_2$ forms uniquely a staggered rotamer, but unlike in the staggered rotamer of $[Ru(bpy)(CO)_2Cl]_2$, the Ru–dmbpy-units are partially

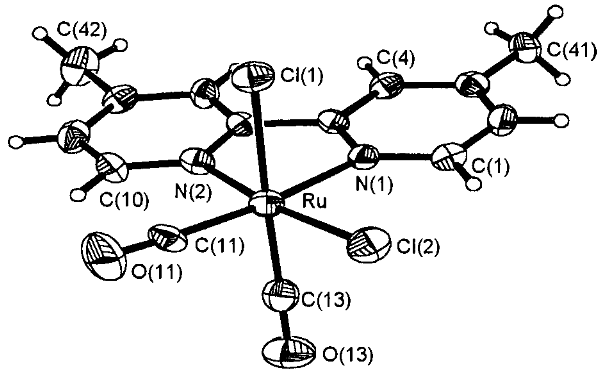

Fig. 4. The structure of Ru(tmbpy)$(CO)_2(Cl)_2$ (**1**).

overlapping (as viewed from the Ru–Ru bond direction in Fig. 4). In this case, it is possible that the arrangement of the bpy units is determined by the bulky methyl groups attached to the bpy rings and the opposing carbonyl ligands by steric and electronic factors.

Despite the excess of the dmbpy ligand used in synthesising complexes **2** and **3**, spectroscopic and crystallographic studies only revealed the formation of mono(2,2′-bipyridine) complexes.

4. Conclusions

Monomeric Ru-mono(2,2′-bipyridine)complexes are known to be precursors for a highly active Ru–bpy catalyst which reduces electrochemically CO_2 and catalyses water gas shift reaction. The detailed characterisation of this compound, which is believed to be polymeric, has not been successful, possibly due to different rotameric substructures in the polymeric Ru–Ru chain. The importance of the structural study of this material lies in the mapping of the different active sites in the metallic backbone of the compound resulting from different rotameric arrangements of both the carbonyl and bipyridine ligands.

In the present study, we have shown that the monomeric precursor of the Ru–bpy polymer can be structurally modified at the bipyridine rings. Ruthenium-mono(bipyridine) derivatives, methylated at the 4,4′ and at the 4,4′-5,5′ sites, have been synthesised and structurally characterised. It has been also demonstrated that the choice of solvent can be used to direct the complexation reaction to dimeric species. The structure of the dimeric methyl substituted complex $[Ru(dmbpy)(CO)_2Cl]_2$ shows how methyl groups in the bipyridine ligands may be used to guide the crystallographic packing in a corresponding dimeric Ru–bpy complex. The bulky sidechains in the 4,4′ positions of the bipyridine ligand locks the rotation and gives an ordered dimeric ruthenium complex. This result may lead to the synthesis of an ordered Ru–bpy polymer and to controlled modification of the catalytically active sites.

4.1. Supporting information available

Tables of atomic positional and *U* parameters, bond lengths and angles, anisotropic displacement coefficients, and *H* coordinates and *U* values for **1–4** and tables of crystallographic data, atomic coordinates and *U* values, bond lengths and angles, and anisotropic displacement coefficients for $[Ru(bpy)(CO)_2Cl]_2$ (in space group *C*2/*m*).

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