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Note

Synthesis and characterization of a tetraruthenium butterfly cluster containing a quadruply-bridging ligand derived from an *N*,*N*′-dipyrid-2-ylurea

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Abstract

The tetraruthenium cluster complex $[Ru_4(\mu_4\text{-}\kappa^4\text{-dmpu})(CO)_{10}]$, H_2dmpu = *N*,*N*′-bis(6-methylpyrid-2-yl)urea, has been prepared by treating $[Ru_3(CO)_{12}]$ with H_2dmpu in toluene at reflux temperature. An X-ray diffraction study has determined that this cluster has a butterfly metallic skeleton hold up by a doubly-deprotonated *N*,*N*′-bis(6-methylpyrid-2-yl)urea ligand (dmpu). This ligand has the pyridine N atoms attached to the wing-tip Ru atoms and the amido N atoms spanning Ru–Ru wing-edges, in such a way that the cluster has C_2 symmetry. The donor atoms of doubly-deprotonated *N*,*N*′-dipyrid-2-ylureas seem to be appropriately arranged to hold butterfly tetranuclear clusters.

Keywords: Ruthenium; Butterfly clusters; *N*,*N*′-Bis(6-methylpyrid-2-yl)urea; *N*,*N*′-Bis(2-picolin-6-yl)urea; *N*,*N*′-Dipyrid-2-ylureas; 2-Amidopyridine ligands

1. Introduction

The coordination chemistry *N*,*N*′-dipyridylureas is expected to be fascinating because they have one oxygen and four nitrogen atoms susceptible to coordinate metal atoms and/or participate in hydrogen-bonding interactions. In addition to their possible behavior as polydentate neutral ligands, their deprotonation may also lead to monoanionic and dianionic ligands. Unfortunately, this promising scenario still needs to be confirmed because, as commented below, the coordination chemistry of *N*,*N*′-dipyridylureas has been little studied.

It has not been until recently that a few papers dealing with reactions of *N*,*N*′-dipyrid-3-ylurea [1] and *N*,*N*′-dipyrid-4-ylurea [2] with transition metal species have been published. These papers demonstrate that such reagents are well suited to act as building blocks to form self-assembled 2D and 3D supramolecular networks.

Regarding *N*,*N*′-dipyrid-2-ylurea (H_2dpu), there are only two reports dealing with transition metal complexes derived from it. The first one describes the serendipitous synthesis of *trans*-$[Ni(NO_3)_2(\kappa^2\text{-}H_2dpu)_2]$ from nickel(II) nitrate, nicotinic acid and 2-aminopyridine [3]. The second paper, describes the preparations of the octahedral complexes *trans*-$[M(NO_3)_2(\kappa^2\text{-}H_2dpu)_2]$ (M = Mn, Fe, Co, Ni, Cu, Zn), $[Fe_2(\mu\text{-}O)(NO_3)_4(\kappa^2\text{-}H_2dpu)_2(MeOH)_2]$ and *mer*-$[Co(\kappa^3\text{-}Hdpu)_2]NO_3$ from H_2dpu and the corresponding metal salts [4].

We now describe that, studying the reactivity of $[Ru_3(CO)_{12}]$ with *N*,*N*′-bis(6-methylpyrid-2-yl)urea (H_2dmpu), we have found that the doubly-deprotonated form of this reagent (dmpu) is capable to induce the formation of a tetranuclear complex with a butterfly metallic skeleton. Although we expected no noticeable differences between the reactivity of H_2dpu and that of its methylated deriva-

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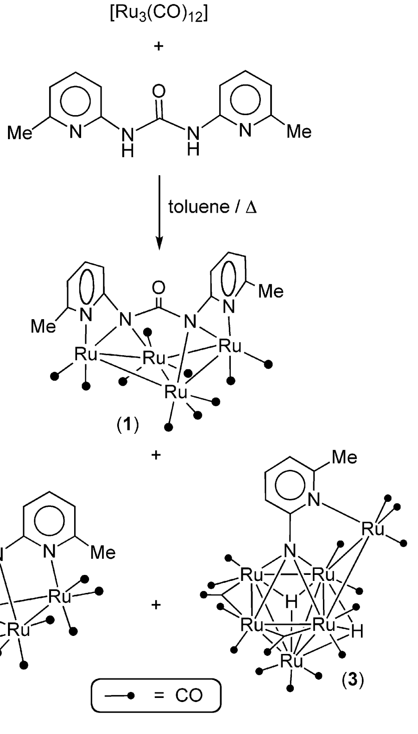
tive H_2dmpu, we preferred to work with the latter because its methyl groups facilitate the monitoring of the reactions by NMR spectroscopy [5].

2. Results and discussion

The reaction of $[Ru_3(CO)_{12}]$ with 0.75 equiv. of H_2dmpu in toluene at reflux temperature slowly gave a mixture of compounds. The heating source was turned off when the IR spectrum of the reaction mixture indicated the consumption of $[Ru_3(CO)_{12}]$ (2 h). A chromatographic workup allowed the separation of the tetranuclear butterfly ruthenium carbonyl cluster $[Ru_4(\mu_4\text{-}\kappa^4\text{-dmpu})(CO)_{10}]$ (**1**; 24%) from small amounts of the known clusters $[Ru_3(\mu\text{-H})(\mu_3\text{-}\kappa^2\text{-Hampy})(CO)_9]$ (**2**; 2%) [6] and $[Ru_6(\mu\text{-H})_2(\mu_5\text{-}\kappa^2\text{-ampy})(\mu\text{-CO})_2(CO)_{14}]$ (**3**; 4%) [7] (Scheme 1). Some untractable dark stuff remained uneluted on the chromatographic support.

The composition of complex **1** was obtained from its CHN microanalysis and positive FAB mass spectrum. The latter contains the peaks of the expected molecular ion isotopomers with their appropriate relative abundance. Its IR spectrum indicates the presence of terminal CO ligands and the absence of NH fragments. Only one 6-methylpyrid-2-yl fragment is shown by its ^{1}H and ^{13}C NMR spectra, the latter also displaying the resonance of the urea carbonyl group (155.8 ppm). These data indicate that the complex has some symmetry and that it contains a new symmetric ligand derived from the double deprotonation of H_2dmpu.



Scheme 1. Reaction of $[Ru_3(CO)_{12}]$ with *N*,*N*′-bis(6-methylpyrid-2-yl)urea.

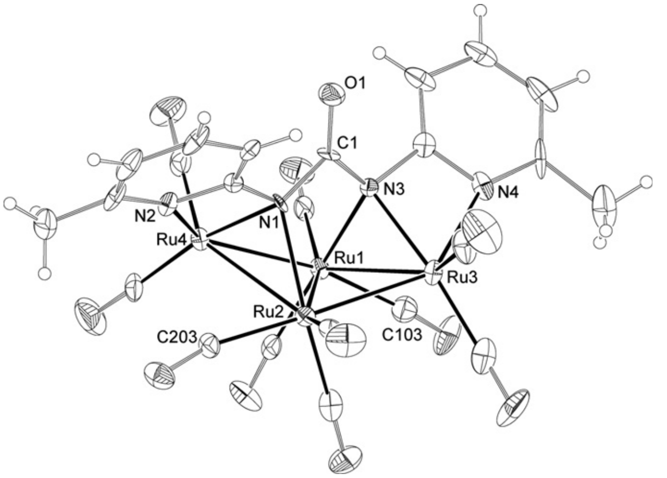


Fig. 1. Molecular structure of compound **1**. Ellipsoids are drawn at the 30% probability level.

Its molecular structure has been determined by X-ray diffraction (Fig. 1, Table 1). The cluster comprises four Ru atoms, 1 dmpu ligand and 10 carbonyl ligands. The metallic skeleton has a butterfly arrangement, being attached to the four N atoms of the dmpu ligand in such a way that the wing-tip Ru atoms Ru(3) and Ru(4) are attached to the pyridine N atoms N(4) and N(2), respectively, and the Ru(1)–Ru(3) and Ru(2)–Ru(4) edges are bridged by the amido N atoms N(3) and N(1), respectively. Each wing-tip Ru atom is attached to two CO ligands, while each hinge Ru atom is attached to three CO ligands. The CO ligands C(103)–O(103) and C(203)–O(203) have a semi-bridging character (Table 1), since they asymmetrically interact with the Ru atoms spanned by the amido N atoms. The remaining CO ligands are clearly terminal. Overall, the molecule has an apparent C_2 symmetry (non-crystallographic). With 62 cluster valence electrons and five Ru–Ru bonds, it obeys the EAN rule.

The clusters $[Ru_3(\mu\text{-H})(\mu_3\text{-}\kappa^2\text{-Hampy})(CO)_9]$(**2**) and $[Ru_6(\mu\text{-H})_2(\mu_5\text{-}\kappa^2\text{-ampy})(\mu\text{-CO})_2(CO)_{14}]$(**3**), which are minor products of this reaction, have been previously prepared by treating $[Ru_3(CO)_{12}]$ with 2-amino-6-methylpyridine (H_2ampy) in 1:1 [6] or 2:1 [7] mol ratio, respectively. We observed that the use of wet toluene for the reaction of $[Ru_3(CO)_{12}]$ with H_2dmpu increased the yields of these by-products. Therefore, even using sodium-dried toluene as solvent, the presence of adventitious moisture in the

Table 1
Selected interatomic distances (Å) in compound 1

Ru(1)–Ru(2)	2.750(2)	Ru(1)–Ru(3)	2.793(3)
Ru(1)–Ru(4)	2.735(2)	Ru(2)–Ru(3)	2.716(2)
Ru(2)–Ru(4)	2.772(2)	N(1)–Ru(2)	2.23(1)
N(1)–Ru(4)	2.14(1)	N(2)–Ru(4)	2.25(1)
N(3)–Ru(1)	2.19(1)	N(3)–Ru(3)	2.11(1)
N(4)–Ru(3)	2.25(1)	C(1)–O(1)	2.20(2)
C(1)–N(1)	1.46(2)	C(1)–N(3)	1.41(2)
C(103)–Ru(1)	1.93(2)	C(103)–Ru(3)	2.61(2)
C(203)–Ru(2)	1.95(2)	C(203)–Ru(4)	2.55(2)

reagents, solvent or glassware, in addition to the small reaction scale, the long reaction time and the high reaction temperature, cause the hydrolysis of H_2dmpu reagent. This produces a small amount of H_2ampy that ends in [Ru_3(μ-H)(μ_3-κ^2-Hampy)$(CO)_9$] and [Ru_6(μ-$H)_2$(μ_5-κ^2-ampy)(μ-$CO)_2(CO)_{14}$].

Quite a few 62-electron butterfly tetraruthenium carbonyl clusters have already been reported. Among them, those containing no hydrocarbon ligands are scarce and have been generally prepared in low yield [8]. The latter always have a bridging ligand that spans two or three metal atoms, e.g. [Ru_4(μ-SR_2)(μ-CO)$(CO)_{12}$] [9] and [Ru_4(μ_3-PR)$(CO)_{13}$] [10].

Although some butterfly tetraruthenium carbonyl clusters containing a quadruply-bridging non-hydrocarbon ligands have been reported, e.g. [Ru_4(μ_4-N)(μ-OMe)$(CO)_{12}$] [11] and [Ru_4(μ_4-$PR)_2(CO)_{12}$] [12], they have more than 62 cluster valence electrons and have no hinge Ru–Ru bond.

Therefore, compound **1** is the first example of a 62-electron butterfly tetraruthenium carbonyl cluster that contains a quadruply-bridging non-hydrocarbon ligand. The particular arrangement of the donor atoms of the dmpu ligand seems to be adequate to induce the coordination of this ligand to butterfly-arranged tetranuclear clusters.

In addition, the coordination mode displayed for the dmpu ligand in compound **1** is unprecedented for dipyrid-2-ylurea derivatives, for which only a chelating behavior has so far been reported [3,4]. Ureas of the type RNHCONHR, in which R is a non-coordinating group, react with [$Ru_3(CO)_{12}$] to give trinuclear derivatives [13].

3. Experimental

3.1. General data

Solvents were dried over sodium diphenylketyl (hydrocarbons) or CaH_2 (dichloromethane) and distilled under nitrogen prior to use. The reactions were carried out under nitrogen, using Schlenk-vacuum line techniques, and were routinely monitored by solution IR spectroscopy and by spot TLC. All reagents were purchased from commercial suppliers. IR spectra were recorded in solution on a Perkin–Elmer Paragon 1000 FT spectrophotometer. ^{1}H and ^{13}C NMR spectra were run on a Bruker DPX-300 instrument, using the CH_2Cl_2 (5.30 ppm, for ^{1}H) or the $CDCl_3$ solvent peaks (77.2 ppm, for ^{13}C) as references. Microanalyses were obtained from the University of Oviedo Analytical Service. FAB-MS were obtained from the University of Santiago de Compostela Mass Spectrometric Service; data given refer to the most abundant molecular ion isotopomer.

3.2. *N,N′-Bis(6-methylpyrid-2-yl)urea*

Although two syntheses of this product have been previously described (reported yields 11% [14] and 57% [15]), we have got a higher yield using a modification of an alternative procedure reported for the synthesis of *N,N′*-dipyrid-2-ylurea [16]. A solution of triphosgene (0.94 g, 3.17 mmol) in dichloromethane (10 mL) was dropwise added, over a period of 1 h, into a solution of 2-amino-6-methylpyridine (1.71 g, 15.81 mmol) and 4-dimethylaminopyridine (2.32 g, 19.00 mmol) in dichloromethane (15 mL). The mixture was stirred for 30 h at room temperature. The solvent was removed under reduced pressure to give a sticky pink solid that was extracted into ethyl acetate (3 × 50 mL). The filtered solution was concentrated to ca. 30 mL and was placed on top of a silica-gel chromatography column (5 × 30 cm) packed in a mixture of hexane and ethyl acetate (1:1). Elution with ethyl acetate afforded a colorless solution that, after a conventional work up, gave *N,N′*-bis(6-methylpyrid-2-yl)urea as a white solid (1.46 g, 76%). Anal. Calc. for $C_{13}H_{14}N_4O$: C, 64.45; H, 5.82; N, 23.12. Found: C, 64.53; H, 5.93; N, 23.08.%. Its spectroscopic data matched those reported in the literature [14].

3.3. *[Ru_4(μ_4-κ^4-dmpu)$(CO)_{10}$] (**1**)*

A mixture of [$Ru_3(CO)_{12}$] (150 mg, 0.235 mmol) and *N,N′*-bis(6-methylpyrid-2-yl)urea (43 mg, 0.177 mmol) was stirred in toluene (10 ml) at reflux temperature for 2 h. Once cooled to room temperature, silica gel (4 g) was added and the solvent was removed under reduced pressure. The solid was placed onto a chromatographic silica gel column (20 × 2.5 cm) packed in hexane. The column was washed with hexane to remove small amounts of [$Ru_3(CO)_{12}$] and [Ru_4(μ-$H)_4(CO)_{12}$] that were not isolated. Hexane–dichloromethane 5:1 eluted five bands. They all were evaporated to dryness to give solid products. The first band, yellow-orange, contained [Ru_3(μ-H)(μ_3-κ^2-Hampy)$(CO)_9$] (3 mg, 2%) [6]. The second band, dark brown, contained [Ru_6(μ-$H)_2$(μ_5-κ^2-ampy)(μ-$CO)_2(CO)_{14}$] (5 mg, 4%) [7]. The third and fourth bands, red and green, respectively, contained trace amounts of unidentified products. The fifth band, dark green, contained compound **1** (40 mg, 24%). A dark brown residue remained uneluted at the top of the chromatographic column. Anal. Calc. for $C_{23}H_{12}N_4O_{11}Ru_4$: C, 29.88; H, 1.31; N, 6.06. Found: C, 29.92; H, 1.36; N, 5.95%. +FAB MS (*m/z*): 926 [M^+]. IR, ν(CO) (CH_2Cl_2): 2061 (m), 2033 (vs), 1998 (s), 1978 (w, sh), 1946 (m), 1924 (w, sh), 1685 (w) cm^{-1}. ^{1}H NMR, δ ($CDCl_3$): 7.78 (t, $J = 7.8$ Hz, 1 H), 7.05 (d, $J = 7.8$ Hz, 1 H), 6.98 (d, $J = 7.8$ Hz, 1 H), 2.41 (s, 3 H) ppm. $^{13}C\{^1H\}$ NMR, δ (DEPT, $CDCl_3$): 210.1 (COs), 202.0 (br, COs), 188.9 (C), 169.3 (C), 155.8 (C=O), 141.0 (CH), 121.8 (CH), 115.1 (CH), 22.9 (CH_3) ppm.

3.4. *X-ray structure of compound **1***

A selection of crystal, measurement and refinement data is given in Table 2. Diffraction data were measured

Table 2
Crystal data and structure refinement details for compound **1**

Formula	$C_{23}H_{12}N_4O_{11}Ru_4$
Formula weight	924.65
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	9.338(6)
b (Å)	26.294(9)
c (Å)	11.834(8)
β (°)	92.10(1)
V (Å^3)	2904(3)
Z	4
$F(000)$	1768
D_{calcd} (g/cm^3)	2.115
Radiation (λ, Å)	Mo Kα (0.71073)
μ (mm^{-1})	2.103
Crystal size (mm)	$0.20 \times 0.04 \times 0.03$
Temperature (K)	296(2)
θ limits (°)	1.55–23.54
Min/max h,k,l	$-10/10, -29/17, -13/13$
Number of reflections collected	12986
Unique reflections	4256
Reflections with $I > 2\sigma(I)$	2229
Absorption correction	SADABS
Max/min transmission	0.942/0.902
Parameters, restraints	370, 0
Goodness-of-fit on F^2	0.939
Final R_1 (on F, $I > 2\sigma(I)$)	0.0749
Final wR_2 (on F^2, all data)	0.1662
Min/max residuals (e/Å^3)	$-1.791/1.288$

at room temperature on a Bruker AXS SMART 1000 diffractometer, using graphite-monochromated Mo Kα radiation. An absorption correction was applied using SADABS [17]. The structure was solved by direct methods and refined by full matrix least-squares against F^2 with SHELXTL [18]. All non-hydrogen atoms were anisotropically refined, except C(11) and N(3) that were persistently non-positive definite on anisotropic refinements and were isotropically refined. All hydrogen atoms were set in calculated positions and refined as riding atoms. The molecular plot was made with the PLATON program package [19]. The WINGX program system [20] was used throughout the structure determination.

Supplementary material

CCDC 650036 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge via http://www.ccdc.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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