DALTON
COMMUNICATION

A new metal–metal bonded diruthenium(II,III) compound bridged by the dianionic tridentate ligand *N*-(2-pyridyl)-2-oxy-5-chlorobenzylaminate (5-Clsalpy^{2-})

Hitoshi Miyasaka,* Chihiro Kachi-Terajima, Tomohiko Ishii and Masahiro Yamashita *

Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, 1-1 Minamiohsawa, Hachioji, Tokyo, 192-0397, Japan. E-mail: miyasaka@comp.metro-u.ac.jp

Received 10th April 2001, Accepted 4th June 2001
First published as an Advance Article on the web 14th June 2001

The ligand-substitution reaction of $Ru_2(O_2CCH_3)_4Cl$ with the tridentate ligand *N*-(2-pyridyl)-2-oxy-5-chlorobenzylaminate dianion (5-Clsalpy^{2-}) led to the unique diruthenium(II,III) compound [{Na(THF)$_2$}{Ru$_2$(O$_2$CCH$_3$)$_2$(5-Clsalpy)$_2$}]·THF (1·THF) which revealed the characteristic 1-D chain structure of the repeating unit [–Na–O–Ru–Ru–O–]$_\infty$ and rich redox chemistry.

Recently, much attention has been paid to the partial ligand-substitution reactions of basic paddlewheel-type metal–metal bonded compounds, for example the carboxylate-bridged type $[M_2(O_2CR)_4]^{n+}$, to form a series of the ligand-substituted compounds $[M_2(O_2CR)_{4-x}(L)_{2x}]^{n+}$ (L = monodentate ligand) and $[M_2(O_2CR)_{4-x}(L)_x]^{n+}$ (L = bidentate or tridentate ligand). This is for the following reasons: i) the electronic configuration of the metal–metal bond can be dramatically varied by changing the bridging ligands;[1] ii) the oxidation state and the redox reaction of the compounds can be directly influenced;[2] iii) the attached ligands, possessing weak coordinating ability as solvent molecules, provide a reaction site for further ligand-substitution;[3] iv) substitution with the inter-unit bridging ligands forms oligomeric systems such as "dimer-of-dimers"[4] and cyclic supramolecular architectures.[5] Regarding ii) above, the use of tridentate ligands, which not only bridge metal ions but can also occupy the axial coordination sites, affords many structural motifs with various metal–metal bond and redox properties.[2,6,7] Nevertheless, instances of metal–metal bonded compounds with tridentate ligands are relatively rare. This is probably due to the difficulty of designing a tridentate ligand which can stabilize a metal–metal bond. We designed dianionic tridentate ligands containing amino-pyridyl and phenolate moieties connected to one another by a methylene group, where the former could attach to the dimetal unit and the latter could flexibly cap the axial (Fig. 1b) or equatorial position (Fig. 1c), as well as monodentate ligands. Here a new metal–metal bonded diruthenium(II,III) compound with *N*-(2-pyridyl)-2-oxy-5-chlorobenzylaminate dianion (5-Clsalpy^{2-}), obtained from the deprotonation of *N*-(2-pyridyl)-2-hydroxy-5-chlorobenzylamine (5-ClsalpyH$_2$; Fig. 1a), which is formulated as [{Na(THF)$_2$}{Ru$_2$(O$_2$CCH$_3$)$_2$(5-Clsalpy)$_2$}]·THF (**1**·THF), will be described.

The bi-ligand-substituted compound **1** was prepared by the reaction of $Ru_2(O_2CCH_3)_4Cl$ with two equivalents of 5-ClsalpyH$_2$, in the presence of four equivalents of NaOH for the deprotonation of the ligand, in degassed methanol, and then crystallized from THF–toluene.† The X-ray crystallographic analysis of **1** revealed that two formula units are included in the asymmetrical unit (triclinic *P*1 with $Z = 4$ as the formula unit), and both Ru$_2$ units are very similar to each other with minor structural differences.‡ Therefore, an ORTEP drawing of only one of the formula units is depicted in Fig. 2a. Each Ru$_2$ unit is composed of two bridging acetate groups and two 5-Clsalpy^{2-} groups, forming the anionic Ru$_2$(II,III) unit, $[Ru_2(O_2CCH_3)_2(5\text{-Clsalpy})_2]^-$. The Ru–Ru bond distances are found to be Ru(1)–Ru(2) = 2.2949(5) Å and Ru(3)–Ru(4) = 2.2898(5) Å which are very close to those observed in $[Ru_2^{II,III}(O_2CR)_4(Cl)]$ and $[Ru_2^{II,III}(O_2CR)_4]^+$ (2.27–2.29 Å).[8] The 5-Clsalpy^{2-} ligands are located in a *trans*-fashion and the phenolate oxygen atoms occupy axial positions to the Ru–Ru vector, as shown in Fig. 1b, with an average bond distance of Ru–O$_{\text{phen}}$ = 2.233(3) Å. The Ru–Ru–phenolate interactions in **1** are denoted by the Ru–Ru–O angles of 174.54(8)° (Ru(2)–Ru(1)–O(1)), 171.60(8)° (Ru(1)–Ru(2)–O(2)), 174.51(8)° (Ru(4)–Ru(3)–O(7)), and 171.49(8)° (Ru(3)–Ru(4)–O(8)) which are more linear than those for previously reported dimetal compounds with tridentate ligands (M–M–L$_{\text{axial}}$ = 159–169°);[2,3] this is because in **1** the coordination mode of the phenolate moiety consists of a flexible six-membered ring, Ru–N–C–C–C–O (see Fig. 1b). The Na$^+$ ions as the counter cation are surrounded by the phenolate oxygen atoms and two acetate oxygen atoms with the support of two THF molecules, forming an alternating one-dimensional chain structure as shown in Fig. 2b.

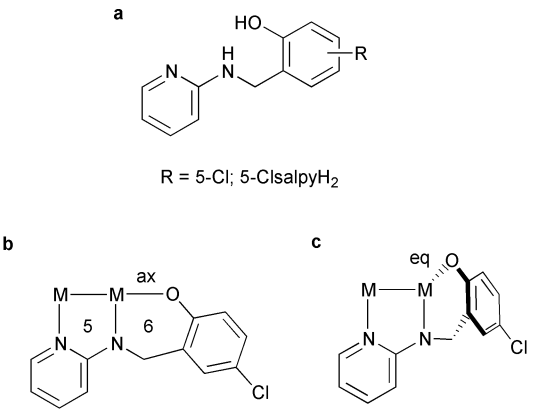

Fig. 1 Schematic drawing of *N*-(2-pyridyl)-2-hydroxy-5-chlorobenzylamine (5-ClsalpyH$_2$; a) and the coordination arrangements of the deprotonated form 5-Clsalpy^{2-} around M–M bonds (b and c). The coordination arrangement (b) was taken in **1**.

The electrochemistry of **1** is one of the characteristic properties which should be mentioned. The electronic behavior of **1** was confirmed by cyclic voltammetry in MeCN containing *n*-Bu$_4$N(PF$_6$) as supporting electrolyte, showing rich redox chemistry especially upon oxidation. One reduction and three oxidations were observed as quasi-reversible waves at $E_{1/2}^{(1,\text{red})} = -1.39$ V, $E_{1/2}^{(1,\text{ox})} = -0.24$ V, $E_{1/2}^{(2,\text{ox})} = 0.34$ V and $E_{1/2}^{(3,\text{ox})} = 0.92$ V, respectively. The one-electron reduction is assigned to the metal-centered $Ru_2^{II,III}/Ru_2^{II,II}$ couple, and the first and second oxidations are assigned to the metal-centered ones, $Ru_2^{III,III}/Ru_2^{II,III}$ and $Ru_2^{III,IV}/Ru_2^{III,III}$, respectively. The dianionic ligands, 5-Clsalpy^{2-}, were able to stabilize the high oxidation state in $Ru_2^{III,IV}$. The third couple is achieved with a two-electron oxidation, which arises from 5-Clsalpy^{2-}-centered oxidations, since the cyclic voltammetry of 5-ClsalpyH$_2$ in MeCN reveals an irreversible one-electron

DOI: 10.1039/b103186b

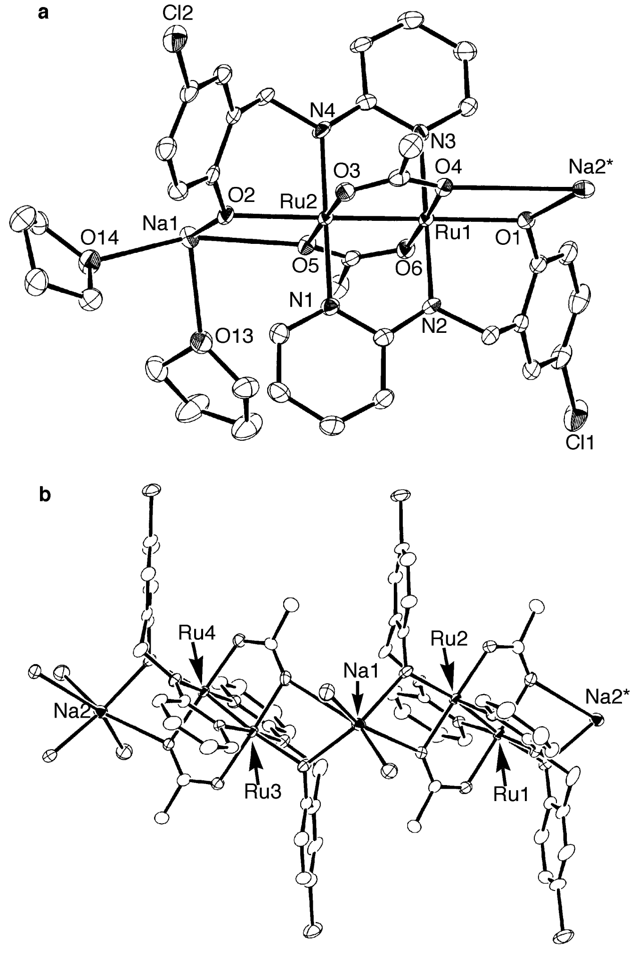

Fig. 2 ORTEP[10] representation of the formula unit of **1** (50% probability level) (a) and a perspective view of the alternating 1-D chain structure of $[\text{–Na–O–Ru–Ru–O–}]_\infty$ (b).

oxidation at $E_\text{p} = 0.68$ V. The phenol radical species could be produced by the oxidation of the 5-Clsalpy^{2-} ligand of **1**. The electronic communication between two phenol radical species *via* the $\text{Ru}_2{}^{\text{III,IV}}$ unit could be small in **1** and correspond to class I of the Robin–Day classification.[9]

In conclusion we present the new bi-ligand-substituted metal–metal bonded diruthenium(II,III) compound **1** containing the dianionic tridentate ligand, 5-Clsalpy^{2-}. Each Ru_2 unit is anionic and forms an alternating 1-D chain structure of $[\text{–Na–O–Ru–Ru–O–}]_\infty$ with Na^+ ions as the counter cations. The $\text{Ru}_2{}^{\text{II,II}}$, $\text{Ru}_2{}^{\text{III,III}}$ and $\text{Ru}_2{}^{\text{III,IV}}$ oxidation states of **1** were newly detected by electrochemistry, and it is very interesting in that the 5-Clsalpy^{2-} ligand was itself oxidized, which may produce phenol radical species. Further investigations of dimetal compounds with salpy^{2-} analogue are now in progress.

Notes and references

† Compound **1**: all synthetic procedures were performed under a dried nitrogen atmosphere. A mixture of 5-ClsalpyH$_2$ (235 mg, 1.0 mmol) and NaOH (80 mg, 2.0 mmol) in 15 cm^3 methanol was added to solid $\text{Ru}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}$ (273 mg, 0.5 mmol) and the brown suspension was stirred for 3 days at room temperature. During this time the brown suspension changed to a dark green solution containing some precipitate. Then, the solution was filtered to remove NaCl and the filtrate was evaporated under reduced pressure at room temperature. To the green solid was added 20 cm^3 THF and the solution filtered to remove NaCl and NaO_2CCH_3. The filtrate (20 cm^3) was put into a narrow Schlenk tube and diffused with 20 cm^3 toluene to form rectangular green crystals of **1**·THF (66%) (Found: C, 45.13; H, 4.21; N, 5.95. $\text{C}_{36}\text{H}_{40}\text{N}_4\text{O}_8\text{Cl}_2\text{Ru}_2\text{Na}$, **1** requires C, 45.37; H, 4.23; N, 5.88%); $\nu_\text{max}/\text{cm}^{-1}$ 2975w, 1605m, 1472s, 1431s, 1368w, 1304m, 1283s, 1051w, 758w, 687w, 666w (KBr pellet); λ_max/nm (MeCN) 318 ($\varepsilon/\text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-1}$ 4230), 466 (4030), 834 (680); $\chi_\text{M}T/\text{cm}^3\ \text{K mol}^{-1}$ 2.10 (300 K), 0.93 (2.0 K).

‡ Crystallographic data for $\text{C}_{40}\text{H}_{48}\text{N}_4\text{O}_9\text{Cl}_2\text{Ru}_2\text{Na}$ **1**·THF, $M = 1024.88$, triclinic, $a = 15.9459(5)$, $b = 22.0822(9)$, $c = 12.7695(5)$ Å, $\alpha = 90.150(2)$, $\beta = 90.138(2)$, $\gamma = 69.2587(7)°$, $U = 4205.0(3)$ Å^3, $T = 100$ K, space group $P\bar{1}$ (no. 2), $Z = 4$, $\mu(\text{Mo-K}\alpha) = 9.14\ \text{cm}^{-1}$, 37111 reflections measured, 18729 unique ($R_\text{int} = 0.036$), refinement method: full-matrix least-squares on F^2. The final R indices: $R_1 = 0.044$ ($I > 3\sigma(I)$), $R = 0.065$, $wR = 0.112$ (all data), GOF = 1.63. CCDC reference number 162350. See http://www.rsc.org/suppdata/dt/b1/b103186b/ for crystallographic data in CIF or other electronic format.

1 The electronic configuration of the series of compounds $[\text{Ru}_2{}^{\text{II,III}}(\text{O}_2\text{CR})_4]^+$ and $[\text{Ru}_2{}^{\text{II,III}}(\text{RNCR'NR})_4]^+$ ($\text{RNCR'NR}^- =$ amidinate) can be generally described as $\sigma^2\pi^4\delta^2(\delta^*\pi^*)^3$ possessing a spin ground state of $S = 3/2$, while $[\text{Ru}_2{}^{\text{II,III}}(\text{RNNNR})_4]^+$ compounds ($\text{RNNNR}^- =$ trianenate) exhibit a spin ground state of $S = 1/2$ supposedly from $\sigma^2\pi^4\delta^2\pi^{*3}$. Consequently, ligand-substitution on the paddlewheel type $\text{Ru}_2{}^{\text{II,III}}$ compounds has the potential to change the electronic configuration. See for example: F. A. Cotton and T. Ren, *Inorg. Chem.*, 1995, **34**, 3190; F. A. Cotton, L. R. Falvello, T. Ren and K. Vidyasagar, *Inorg. Chim. Acta*, 1992, **194**, 163.

2 J. L. Bear, Y. Li, B. Han, E. V. Caemelbecke and K. M. Kadish, *Inorg. Chem.*, 2001, **40**, 182; J. L. Bear, Y. Li, B. Han, E. V. Caemelbecke and K. M. Kadish, *Inorg. Chem.*, 1996, **35**, 3053; T. Ren. V. DeSilva, G. Zou, C. Lin, L. M. Daniels, C. F. Campana and J. C. Alvarez, *Inorg. Chem. Commun.*, 1999, **2**, 301.

3 G. Pimblett, C. D. Garner and W. Clegg, *J. Chem. Soc., Dalton Trans.*, 1986, 1257; K. V. Catalan, D. J. Mindiola, D. L. Ward and K. R. Dunbar, *Inorg. Chem.*, 1997, **36**, 2458; K. R. Dunbar, *J. Am. Chem. Soc.*, 1988, **110**, 8247; S. L. Bartley, S. N. Bernstein and K. R. Dunbar, *Inorg. Chim. Acta*, 1993, **213**, 213.

4 R. H. Cayton, M. H. Chisholm, J. C. Huffman and E. B. Lobkovsky, *J. Am. Chem. Soc.*, 1991, **113**, 8709; M. H. Chisholm, *Acc. Chem. Res.*, 2000, **33**, 53; R. H. Cayton, M. H. Chisholm, E. F. Putilina and K. Folting, *Polyhedron*, 1993, **12**, 2627; F. A. Cotton, C. Li and C. A. Murillo, *J. Chem. Soc., Dalton Trans.*, 1998, 3151; J. K. Bera, P. Angaridis, F. A. Cotton, M. A. Petrukhina, P. E. Fanwick and R. A. Walton, *J. Am. Chem. Soc.*, 2001, **123**, 1515; F. A. Cotton, L. M. Daniels, G. T. Jordan IV, C. Lin and C. A. Murillo, *Inorg. Chem. Commun.*, 1998, **1**, 109; F. A. Cotton, L. M. Daniels, G. T. Jordan IV, C. Lin and C. A. Murillo, *J. Am. Chem. Soc.*, 1998, **120**, 3398; F. A. Cotton, L. M. Daniels, I. Guimet, R. W. Henning, G. T. Jordan IV, C. Lin, C. A. Murillo and A. J. Schultz, *J. Am. Chem. Soc.*, 1998, **120**, 12531; F. A. Cotton, J. P. Donahue, C. Lin and C. A. Murillo, *Inorg. Chem.*, 2001, **40**, 1234.

5 F. A. Cotton, L. M. Daniels, C. Li and C. A. Murillo, *J. Am. Chem. Soc.*, 1999, **121**, 4538; F. A. Cotton, L. M. Daniels, C. Li and C. A. Murillo, *Chem. Commun.*, 1999, 841; F. A. Cotton, L. M. Daniels, C. Lin, C. A. Murillo and S.-Y. Yu, *J. Chem. Soc., Dalton Trans.*, 2001, 502; F. A. Cotton, C. Lin and C. A. Murillo, *Inorg. Chem.*, 2001, **40**, 575; F. A. Cotton, C. Li and C. A. Murillo, *Inorg. Chem.*, 2001, **40**, 478; F. A. Cotton, C. Li and C. A. Murillo, *Inorg. Chem.*, 2001, **40**, 472; R. P. Bonar-Law, T. D. McGrath, N. Singh, J. F. Bickley and A. Steiner, *Chem. Commun.*, 1999, 2457.

6 W. R. Tikkanen, E. Binamira-Soriaga, W. C. Kaska and P. C. Ford, *Inorg. Chem.*, 1984, **23**, 141.

7 C. S. Campos-Fernández, X. Ouyang and K. R. Dunbar, *Inorg. Chem.*, 2000, **39**, 2432.

8 F. A. Cotton and R. A. Walton, *Multiple Bonds Between Metal Atoms*, Oxford University Press, Oxford, 2nd edn., 1993.

9 M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 247.

10 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.