

Available online at www.sciencedirect.com



INORGANIC CHEMISTRY COMMUNICATIONS

Inorganic Chemistry Communications 10 (2007) 948-951

www.elsevier.com/locate/inoche

Two-way synthesis of a double-lantern heterobimetallic complex $[Pd(\mu-OOCMe)_4Co]_2(\mu-OOCMe)_2Pd(py)_2$

Sergei E. Nefedov^a, Ilya A. Yakushev^a, Natalia Yu. Kozitsyna^a, Zhanna V. Dobrokhotova^a, Vladimir N. Ikorsky^{b,‡}, Michael N. Vargaftik^{a,*}, Ilya I. Moiseev^a

^a N.S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninsky prospect 31, 119991 Moscow, Russian Federation ^b International Tomographic Center, Siberian Branch, Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation

> Received 28 March 2007; accepted 6 May 2007 Available online 18 May 2007

Abstract

The lantern complex $Pd^{II}(\mu$ -OOCMe)₄Co^{II}(NCMe) (1) was transformed into the pentanuclear double-lantern acetate-bridged heterobimetallic complex $[Pd(\mu$ -OOCMe)₄Co]₂(μ -OOCMe)₂Pd(py)₂ (py is pyridine) (2) by two routes: (i) reaction of 1 with pyridine and (ii) reaction of 1 with *trans*-Pd(py)₂(OOCMe)₂. Complex $2 \times 3C_6H_6$ was characterised by single-crystal X-ray diffraction, DTA-TG and magnetic susceptibility data.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Heterobimetallic acetate complexes; Palladium; Cobalt; Pyridine; X-ray structure; Magnetic susceptibility; Thermogravimetry

Palladium(II)-based heterometallic complexes containing transition metals attract attention as potential precursors for the preparation of mixed-metal catalysts and nanomaterials [1,2]. Recently we have synthesised and structurally characterised a series of heterobimetallic Pd^{II}-based lantern-type complexes of the general formula Pd^{II}M^{II}(µ-OOCMe)₄L $(M = Mn, Co, Ni, Zn; L = H_2O, MeCN)$ [3]. In these complexes the Pd^{II} and M^{II} atoms are drawn together by four acetate bridges, so that the Pd \cdots M distances (2.46–2.68 Å) are close to the sum of covalent radii, implying some metal-metal interaction. Such a structure is favourable for keeping together the constituent metal atoms during chemical and thermal transformations. For example, the complex $Pd^{II}Zn^{II}(\mu$ -OOCMe)₄(OH₂) was easily reduced with H₂ to afford a catalytically active PdZn nanoalloy under fairly mild conditions (10% H₂/He, 150 °C) [4].

The labile axial ligands L = MeCN or H_2O bound to the pentacoordinated metal atom were expected to be easily replaced by stronger monodentate O,N-bases without any noticeable change in the complex structure. We have previously found that bidentate 1,10-phenanthroline (phen) reacts with the complex $Pd^{II}Co^{II}(\mu$ -OOCMe)₄(NCMe) (1) in such a way that phen attaches to the cobalt(II) rather than to the palladium(II) atom [5], substituting the axial MeCN ligand and breaking one of four acetate bridges and producing a triply bridged complex (MeCOO)Pd- $(\mu$ -OOCMe)₃Co(phen) in which a rather short Pd···Co distance in the Pd(μ -OOCMe)₃Co moiety (2.69 Å) was only slightly elongated compared to 1. Continuing our studies of the reactivity of the Pd^{II}-based heterobimetallic complexes, we checked the strength of the quadruply bridged Pd^{II}(µ-OOCMe)₄Co^{II} system in reactions with other N-bases.

Here we report the reaction of 1 with a monodentate N-base, pyridine (py). Based on the precedent reaction of 1 with 1,10-phenanthroline, the pyridine molecule was expected to readily substitute the axial ligand L = MeCN

^{*} Corresponding author. Tel.: +7 495 9554865; fax: +7 495 9541279. *E-mail address:* wahr36@mail.ru (M.N. Vargaftik).

[♣] Deceased.

^{1387-7003/\$ -} see front matter @ 2007 Elsevier B.V. All rights reserved. doi:10.1016/j.inoche.2007.05.004

in 1, while the quadruply bridged $Pd^{II}(\mu$ -OOCMe)₄Co^{II} moiety will not be corrupted. However, we unexpectedly found that this reaction [6], unlike that with phen, produced a new complex $[Pd(\mu$ -OOCMe)₄Co]₂(μ -OOCMe)₂-Pd(py)₂ (2).

The reaction suggests that a portion of 1 undergoes a nucleophilic attack by py on the Pd atom to break the quadruply bridged Pd(OOCMe)₄Co system, producing a virtual mononuclear diacetato-bis(pyridine)palladium(II) species. The latter reacts with the rest molecules 1, substituting the labile axial MeCN ligand by the donor O atom of the coordinated MeCOO group and linking two molecules of 1 into pentanuclear complex 2. To verify this suggestion, we performed a direct reaction between 1 and separately prepared *trans*-Pd(py)₂(OOCMe)₂. The reaction [7] also afforded 2 in good yield. In both the cases 2 was isolated from the reaction solution as the crystal solvate $2 \times 3C_6H_6$.

Hence, complex **2** was prepared by two methods: (i) reaction of **1** with py and (ii) reaction of **1** with the complex trans-Pd(py)₂(OOCMe)₂ :

THF (Pd–O: 1.999(3) Å; Pd–N: 2.029(4) Å) [10]. The single pentanuclear carboxylate-bridged mixed-metal complex with similar structure $[Cu(\mu-OOCH_2Cl)_4Y]_2Cu(ClCH_2-COO)_8(H_2O)_8$ that is known to us was isolated from the reaction of mononuclear copper and yttrium nitrates with sodium chloroacetate in aqueous solution [11].

This work demonstrates an example of the design of multinuclear mixed-metal complexes using a mononuclear carboxylate metal complex as the linking agent for heterobimetallic lantern complexes bearing a labile donor ligand or a vacant orbital.

Molecules 2 are connected in the crystal $2 \times 3C_6H_6$ through weak contacts of the lantern Pd atoms with one of three solvate C_6H_6 molecules, forming infinite 1D chains (Pd···C ≈ 3.1 Å) (Fig. 2), while two other C_6H_6 molecules of crystallization are located in the crystal voids and have no close contacts with molecules 2.

Complex 2 is paramagnetic [12]. The effective magnetic moment decreases monotonically from 7.21 to 5.18 MB in the temperature interval 300-2 K corresponding to two magnetically independent Co^{II} centers with spin 3/2 and



i: benzene, room temperature (yield 40%) *ii*: benzene, room temperature (yield 65%)

X-ray crystallography [8] (Fig. 1) showed that molecule **2** consists of two heterodinuclear lantern moieties PdCo $(\mu$ -OOCMe)₄ (Pd–O: 2.000(3)–2.010(3) Å; Co–O: 2.060(3)–2.085(3) Å) connected to each other through two bridging acetate ligands (Co(1)–I(9): 2.003(3) Å) belonging to the central *trans*-Pd(py)₂(OOCMe)₂ linker (Pd–O: 2.011(2) Å; Pd–N: 2.022(3) Å). The Pd–Co distance in molecule **2** (Pd···Co: 2.5418(7) Å) is practically the same as that in molecule **1** (Pd···Co 2.515(3) Å, 2.551(3) Å in two independent molecules in crystal **1**).

The bond distances in the central fragment Pd(OOC-Me)₂(py)₂ are close to those in **1**, *trans*-Pd(py)₂ (OOC-Me)₂ × H₂O (Pd-O: 2.009(3) Å; Pd-N: 2.021(3) Å) [9] and the adduct Pd(OOCMe)₂(py)₂ × {Pd(py)₄[B(C₆F₅)2]} ×

a substantial contribution of spin–orbital interactions and intermolecular antiferromagnetic exchange at low temperatures (Fig. 3).

Crystals $2 \times 3C_6H_6$ easily lose the solvation C_6H_6 molecules upon storage in air at room temperature for 6–10 h. The DTA-TG study [13] showed that complex 2 (free of the solvation C_6H_6) is stable upon heating to 90 °C under Ar. Further heating under Ar produced (i) elimination of one py ligand at 90–160 °C (weight loss 6.9% with a weak endotherm); (ii) rearrangement of 2 after the loss of one py ligand and the elimination of about half of MeCOO ligands at 160–190 °C (weight loss 25.2% with a strong two-stage endotherm); (iii) elimination of the second py ligand at 190–250 °C (weight loss 6.0% without noticeable thermal



Fig. 1. Molecular structure of complex 2 with hydrogen atoms omitted for clarity. The thermal ellipsoids are shown at 50% probability (symmetry transformations used to generate equivalent atoms: #1 - x, -y, -z; #2 - x + 1, y - 1, -z + 1).



Fig. 2. Fragment of a chain formed by molecules 2 linked through a solvate benzene molecule in the crystal $2 \times 3C_6H_6$.



Fig. 3. Magnetic susceptibility of complex 2 in the range 2–300 K.

effect); (iv) final decomposition in the interval 250–380 °C (weight loss 29.0% with complex thermal effects). The total weight loss upon heating to 500 °C ($61.1 \pm 1.5\%$) corre-

sponds to transformation of **2** to Pd metal and CoO (calculated weight loss 60.4%). XRD [14] confirmed that the final products of decomposition of **2** at 500 °C are Pd metal and CoO. The reflections from Pd metal and CoO crystallytes are rather broad. Based on the most intense lines (111) and (200), the average sizes of the Pd and CoO crystallites were estimated by the Scherrer equation $\beta = K\lambda/L\cos\theta$ as at most 5–10 nm. Hence, the solid material produced by thermal decomposition of **2** seems to consist of the Pd metal and CoO rate Pd metal produced by the solid material produced by the Pd metal and CoO nanoparticles.

Acknowledgements

The authors thank the financial support from the Russian Foundation for Basic Research (Projects nos. 05-03-32983, 06-03-32578, 06-03-32742 and 06-03-08173), the Foundation of President of the Russian Federation (program for Support of Leading Russian Scientific Schools, grant NSh-4959.2006.03) and the Russian Academy of Sciences (programs for Basic Research "Purposeful Synthesis of Inorganic Substances and Creation of Related Functional Materials" and "Theoretical and experimental investigation of the nature of chemical bonding and mechanisms of important reactions and processes").

Appendix A. Supplementary material

CCDC 641937 contains the supplementary crystallographic data for $2 \times 3C_6H_6$. These data can be obtained free of charge via http://www.ccdc.cam.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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche. 2007.05.004.

References

- J.M. Thomas, W.J. Thomas, Principles and Practice of Heterogeneous Catalysis, VCH, New York, 1997.
- [2] J.H. Sinfelt, Bimetallic Catalysts. Discoveries, Concepts and Applications, Wiley, New York, 1983.
- [3] N.Yu. Kozitsyna, S.E. Nefedov, F.M. Dolgushin, N.V. Cherkashina, M.N. Vargaftik, I.I. Moiseev, Inorg. Chim. Acta 359 (2006) 2072–2086.
- [4] O.P. Tkachenko, A.Yu. Stakheev, L.M. Kustov, I.V. Mashkovsky, M. van den Berg, W. Grünert, N.Yu. Kozitsyna, Zh.V. Dobrokhotova, V.I. Zhilov, S.E. Nefedov, M.N. Vargaftik, I.I. Moiseev, Catal. Lett. 112 (2006) 155–161.
- [5] S.E. Nefedov, M.N. Vargaftik, I.I. Moiseev, Inorg. Chem. Commun. 9 (2006) 755–757.
- [6] Synthesis of 2 by method 1. To a suspension of PdCo(OOC-Me)₄(NCMe) (210 mg, 0.5 mmol) (prepared according to [3]) in benzene (15 ml) was added pyridine (40 mg, 0.5 mmol) under stirring. The reaction mixture was magnetically stirred for 15 min at room temperature to produce a purple solution, which was filtered and kept for crystallization for 12 h at room temperature. The purple-red crystals of $2 \times 3C_6H_6$ were separated from the mother liquor and used for X-ray diffraction study. An additional portion of fine-crystalline $2 \times 3C_6H_6$ was obtained after storage of the mother liquor at +15 °C for 24 h. Total yield: 94 mg (40% based on Pd). Anal. for $2 \times 3C_6H_6$: Found (%): C, 40.52; H, 4.18; N, 2.03. Pd₃Co₂C₄₈O₂₀H₅₈N₂. Calc. (%): C, 40.60; H, 4.12; N, 1.97. The crystals of $2 \times 3C_6H_6$ readily lose the crystallization benzene molecules after storage in air at room temperature for 6–10 h. Anal. for 2 (free of C_6H_6): Found (%): C, 30.67; H, 3.58; N, 2.13. Pd₃Co₂C₃₀O₂₀H₄₀N₂. Calc. (%): C, 30.39; H, 3.40; N, 2.36. IR (KBr), v/cm⁻¹: 2986w, 1622s, 1576w, 1552m, 1451w, 1405vs, 1341m, 1211w, 1150w, 1072w 1026w, 764m, 716w, 696s, 624m.
- [7] Synthesis of 2 by method 2. The complex *trans*-Pd(py)₂(OOCMe)₂ was prepared according to [9] and used without separation from the reaction mixture. Pyridine (32 mg, 0.4 mmol) was added to a solution

of Pd₃(OOCMe)₆(50 mg, 0.2 mmol based on Pd) in benzene (10 ml) and the reaction mixture was magnetically stirred at room temperature for 15 min until a light-yellow precipitate of *trans*-Pd(py)₂-(OOCMe)₂ × H₂O formed. A solution of PdCo(OOCMe)₄(NCMe) (212 mg, 0.48 mmol, 20% excess) in benzene (15 ml) was added to this suspension and magnetically stirred for 0.5 h to produce a purple solution. The solution was filtered and kept for crystallization at room temperature for 24 h. The crystals of $2 \times 3C_6H_6$ were separated from the mother liquor and used for X-ray diffraction study. An additional portion of $2 \times 3C_6H_6$ was obtained by precipitation with hexane. Total yield 206 mg (65% based on Pd). Anal. for 2 (free of C_6H_6): Found (%): C, 30.56; H, 3.48; N, 2.23. Pd₃Co₂C₃₀O₂₀H₄₀N₂. Calc. (%): C, 30.39; H, 3.40; N, 2.36. IR (KBr), *v*/cm⁻¹: 2984w, 1621s, 1576w, 1552m, 1450w, 1405vs, 1340m, 1211w, 1150w, 1071w 1026w, 764m, 716w, 695s, 624m.

- [8] X-ray structure analysis of $2 \times 3C_6H_6$: Bruker AXS SMART 1000, CCD-detector λ (Mo K α) = 0.71073 Å, graphite monochromator, ω scanning, $2\theta_{max} = 54^{\circ}$. $C_{48}H_{58}Co_2N_2O_{20}Pd_3$, M = 663.82, triclinic, space group $P\bar{1}$, a = 8.2681(18) Å, b = 10.465(2) Å, c = 16.421(4) Å, $\alpha = 98.692(8)^{\circ}$, $\beta = 97.223(7)^{\circ}$, $\gamma = 91.174(8)^{\circ}$, V = 1392.2(5) Å³ (110E), Z = 1, $D_{calc} = 1.694$ g/cm³, 12364 measured reflections, 4684 independent reflections with $F^2 > 2\sigma(I)$, $\mu = 1.607$ cm⁻¹, $R_1 = 0.0439$, $wR_2 = 0.1071$. Corrections for absorption were made by SADABS [16]. The structure was solved by the direct method and refined by the full-matrix least squares method for F^2 with anisotropic parameters for all non-hydrogen atoms. All calculations were performed with the use of the SAINT [17] and SHELXTL-97 [18] program packages.
- [9] S.V. Kravtsova, I.P. Romm, A.I. Stash, V.K. Belsky, Acta Crystallogr. C 52 (1996) 2201–2204.
- [10] Liging Ma, R.C. Smith, J.D. Protasiewicz, Inorg. Chim. Acta 358 (2005) 3478–3482.
- [11] Cun-Gen Zhang, Deyue Yan, Yilin, Fengyue. Yang, J. Coord. Chem. 51 (2000) 261–269.
- [12] Magnetic susceptibility was measured on a SQUID magnetometer MPMS-XL "Quantum Design" in the temperature interval 2–300 K at a magnetic field strength of 5000 Oe.
- [13] DTA-TG measurements were performed on DSC-20 and TG-50 units of a thermoanalyzer TA-3000 (Mettler) under argon with a rate of 5° min⁻¹.
- [14] XRD was studied on a focusing Guinier camera FR-552 (Cu K α l radiation, germanium as an the internal standard). The diffraction pattern was measured on a comparator IZA-2 (LOMO, St.-Petersburg, Russia) with an accuracy of 0.01 mm and indexed using the program TREOR 90 [15].
- [15] P.-E. Werner, L. Eriksson, M. Westdahl, J. Appl. Crystallogr. 18 (1985) 367–370.
- [16] G.M. Sheldrick, SADABS, 1997, Bruker AXS Inc., Madison, WI-53719, USA.
- [17] SMART V5.051 and SAINT V5.00, Area detector control and integration software, 1998, Bruker AXS Inc., Madison, WI-53719, USA.
- [18] G.M. Sheldrick, SHELXTL-97 V5.10, 1997, Bruker AXS Inc., Madison, WI-53719, USA.