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Molecular Assembly with Axial Cyanato Ligands and Paddlewheel Tetracarboxylatodiruthenium(II,III) Fragments

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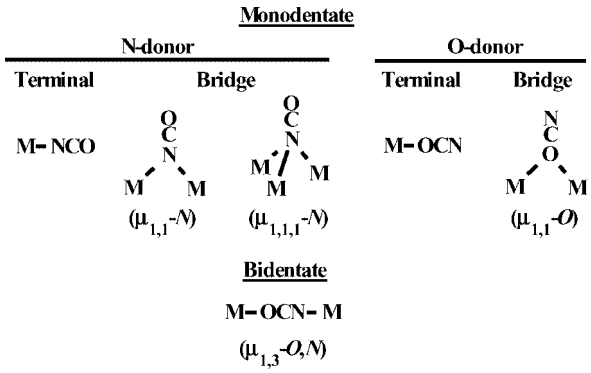
Homo and heteropolymetallic chains constructed with $[Ru_2(\mu\text{-}O_2CR)_4]^+$ building blocks and OCN^- and $[Ag(OCN)_2]^-$ connectors are described. In the complexes $[Ru_2\{\mu\text{-}O_2CC(Me)=CHEt\}_4(OCN)]_n$ (**1**) and $\{[Ru_2(\mu\text{-}O_2CMe)_4][Ag(OCN)_2]\}_n$ (**2**) an infrequent $\mu_{1,1}$-*O* coordination mode of the OCN^- ligand is observed. In addition, the formation of a Ag–OCN bond instead of the Ag–NCO coordination mode, which is more usual, is noteworthy in complex **2**.

Introduction

The use of M_2 paddlewheel species as building blocks to construct polynuclear assemblies has focused great interest in recent years due to the potential applications of these assemblies.[1–3] Especially, the preparation of supramolecular structures based on diruthenium cores has attracted much attention because of the singular electronic and magnetic properties of these structures.[4–7] Thus, numerous polymeric or molecular arrangements with tetracarboxylatodiruthenium(II,III) units that are linked by mononegative anions, neutral molecules or organic radicals have been described.[4,5] However, in spite of the fact that pseudohalide ligands represent an efficient way to generate interactions between metallic centres, these ligands have been little used to connect diruthenium units. Some thiocyanato complexes have been described,[8] but the cyanate group has not been used previously in this chemistry.

The cyanate group is a very versatile ligand that can be bonded in several ways. In Scheme 1 are collected the main coordination modes of this ligand. The N-bonded monodentate mode is the most usual, whereas $\mu_{1,1}$-*O* coordination has been scarcely observed.

On the other hand, the design of heteropolynuclear complexes combining the electronic and stereochemical peculiarities of two different metal ions is a very attractive strategy in obtaining complexes with interesting magnetic, electronic or electric properties.[9]



Scheme 1. Main coordination modes of the cyanato ligand.

In this communication we describe the formation of chains constructed by using $[Ru_2(\mu\text{-}O_2CR)_4]^+$ fragments and OCN^- groups. The preparation of one heteropolynuclear species containing diruthenium and silver centres is also described.

Results and Discussion

Treatment of $[Ru_2\{\mu\text{-}O_2CC(Me)=CHEt\}_4]BF_4$[10] with 5 equiv. sodium cyanate in methanol/water gives brown crystals of $[Ru_2\{\mu\text{-}O_2CC(Me)=CHEt\}_4(OCN)]_n$ (**1**). The X-ray crystal structure of **1** is shown in Figure 1.

This structure has two Ru atoms linked by four *trans*-2-methyl-2-pentenoato bridging ligands; the axial positions are occupied by cyanate groups, giving zigzag chains. These cyanato ligands are coordinated by an infrequent $\mu_{1,1}$-*O* coordination mode. The Ru–Ru and Ru–O_{axial} distances are 2.2793(13) and 2.258(5) Å respectively, typical of those

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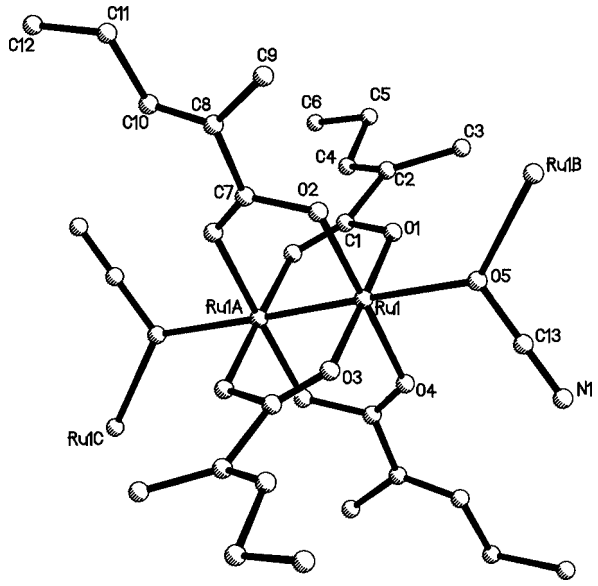

Figure 1. PLUTO view of $[Ru_2\{\mu\text{-}O_2CC(Me)=CHEt\}_4(OCN)]_n$ (**1**). Hydrogen atoms are omitted for clarity.

found in other polymeric complexes with O-donor bridging ligands.[4,5,11] The Ru–O–Ru angle [131.0(6)°] is larger than those found[4,5] in other nonlinear one-dimensional supramolecular structures formed with other bridging ligands. In contrast, the parent chlorido derivative $[Ru_2Cl\{\mu\text{-}O_2CC(Me)=CHEt\}_4]_n$ shows[10] an arrangement of linear chains in the solid state.

A methanol/water solution obtained from the reaction of $[Ru_2Cl(\mu\text{-}O_2CMe)_4]$ with $AgNO_3$ was treated again with 1 equiv. silver nitrate, and 2 equiv. sodium cyanate to give $\{[Ru_2(\mu\text{-}O_2CMe)_4][Ag(OCN)_2]\}_n$ (**2**). The crystal structure of **2** has been determined, and a PLUTO view is shown in Figure 2.

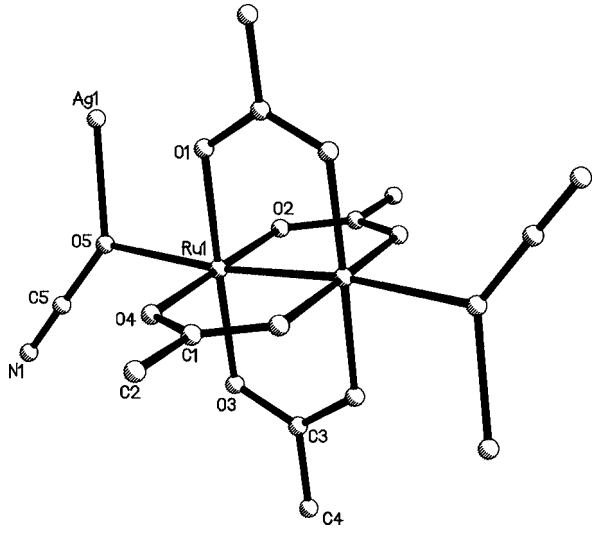

Figure 2. PLUTO view of $\{[Ru_2(\mu\text{-}O_2CMe)_4][Ag(OCN)_2]\}_n$ (**2**). Hydrogen atoms are omitted for clarity.

This compound is formed by zigzag chains that could be considered as $[Ru_2(\mu\text{-}O_2CMe)_4]^+$ units linked by $[Ag(OCN)_2]^-$ groups. The cyanato ligands display the same $\mu_{1,1}$-*O* coordination mode as those in complex **1**, but in this case they bridge the ruthenium and silver atoms (Figure 3).

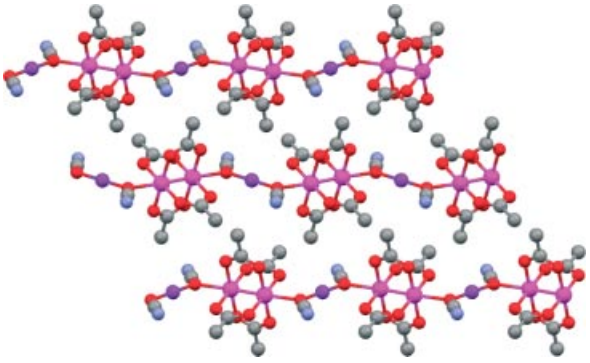

Figure 3. Packing of the zigzag chains of $\{[Ru_2(\mu\text{-}O_2CMe)_4][Ag(OCN)_2]\}_n$ (**2**). Hydrogen atoms are omitted for clarity.

The Ru–Ru bond length is 2.2740(9) Å, and the Ru–$O_{cyanate}$ bond length is 2.271(6) Å. The Ru–O–Ag angle [106.0(2)°] is smaller than the Ru–O–Ru angle in **1**.

An end-to-end (Ru–OCN–Ag) coordination mode for the cyanate group was expected in complex **2**, because the OCN^- ligand is N-bonded in all the structures described[12] for silver complexes. The only exception is the compound $[Ag_2(NCO)_2(dpph)_2]$ [dpph = bis(diphenylphosphanyl)hexane], in which a $\mu_{1,3}$-*N*,*O* coordination mode has been found.[12b] Complex **2** is the first example where the cyanato ligand is coordinated to a silver centre by the oxygen atom, leaving the nitrogen atom uncoordinated. It is also noteworthy that the oxygen atom is shared with the neighbouring ruthenium atom to give $\mu_{1,1}$-*O* coordination. These results contrast with the existence of isocyanato ligands in the complex[13] $(NBu_4)[Ag(NCO)_2]$.

The magnetic measurements of both compounds show magnetic moments at room temperature corresponding to the presence of three unpaired electrons per diruthenium unit. These magnetic moments, 3.69 and 4.15 μ_B for **1** and **2** respectively, are in accordance with the ground-state configuration $\sigma^2\pi^4\delta^2(\pi^*\delta^*)^3$ proposed by Norman et al.[14] The representation of the magnetic moment vs. temperature shows a decrease in the magnetic moment, mainly at low temperatures (Figure 4).

The molar magnetic susceptibility increases continuously with decreasing temperature. This behaviour has been observed in other zigzag polymeric diruthenium(II,III) compounds and is due to a large zero-field splitting (ZFS) and a weak degree of antiferromagnetic coupling between the dimetallic units.[4–6,11] The magnetic moments for **1** are considerably lower than those for **2** in the whole temperature range. This behaviour indicates the existence of a stronger antiferromagnetic interaction in **1**. In order to estimate the *zJ* values, we have fitted the experimental magnetic data by using the model of Cukiernik et al.,[15] which incorporates

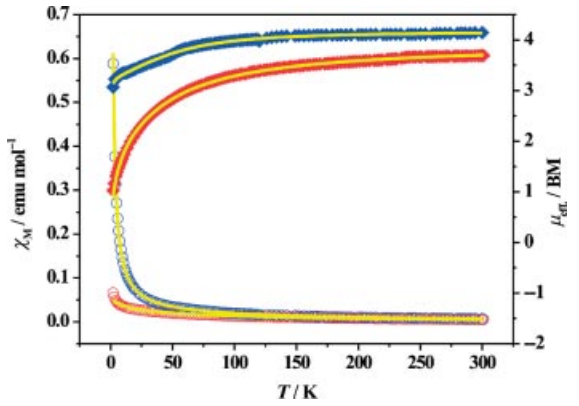

Figure 4. Temperature dependence of the molar magnetic susceptibility (●) and magnetic moment (♦) for **1** (red) and **2** (blue). The solid lines result from least-squares fits with $g = 2.0$, $D = 44.6$ cm^{-1}, $zJ = -5.0$ cm^{-1} for **1** and $g = 2.2$, $D = 64.0$ cm^{-1}, $zJ = -0.1$ cm^{-1} for **2**.

a strong ZFS as well as a weak intermolecular antiferromagnetism by the molecular field approximation. However, for complex **1** better parameters have been obtained with our model,[16] which introduces into the spin Hamiltonian the ZFS and a strong antiferromagnetic interaction. The fits of the experimental data (Figure 4) confirm the presence of a higher magnetic interaction for **1** (–5.0 cm^{-1}) than for **2** (–0.1 cm^{-1}). This behaviour could be explained on the basis of two factors: i) the different distances between the diruthenium units in **1** and **2** or ii) the nature of the linker OCN^- or $[Ag(OCN)_2]^-$. However, a strong antiferromagnetic coupling between Ru_2(II,III) units with a long linker has been found by Ren et al.[17] Thus, although Ren's complex and **2** are different, we think that the difficulty of the electronic exchange through the diamagnetic $[Ag(OCN)_2]^-$ group is probably the main factor in the low magnetic coupling in complex **2**.

Conclusions

The present work describes the first diruthenium units linked by OCN^- or $[Ag(OCN)_2]^-$ groups that show an unusual $\mu_{1,1}$-*O* coordination mode. The design strategies reported in this communication lead to chains with a better magnetic interaction through the OCN^- group than the $[Ag(OCN)_2]^-$ fragment. Our further work will explore the preparation of one-dimensional supramolecular structures formed by diruthenium units and anionic metallic cores.

Experimental Section

General Remarks: All reactions were carried out in an inert atmosphere, by using standard Schlenk techniques. The complexes $[Ru_2Cl(\mu\text{-}O_2CMe)_4]$ and $[Ru_2\{\mu\text{-}O_2CC(Me)=CHEt\}_4]BF_4$ were prepared by literature procedures.[10,18] Other chemicals and solvents were obtained from commercial sources and used without further purification.

Elemental analyses were carried out by the Microanalytical Service of the Complutense University of Madrid. IR spectra were recorded with a Midac prospect FT-IR, or a Shimadzu FT-IR Prestige-21 spectrophotometer by using KBr discs. The variable-temperature magnetic susceptibility data were measured with a Quantum Design MPMS*XL* SQUID (Superconducting Quantum Interference Device) susceptometer over a temperature range of 2 to 300 K. All data were corrected for the diamagnetic contribution of both the sample holder and the compound to the susceptibility. The molar diamagnetic corrections for the complexes were calculated on the basis of Pascal's constants. Mass spectra were obtained with a Bruker Esquire-LC with Electrospray Ionization (ESI) by using methanol or dmso as solvent. Nominal molecular masses and isotopic distribution of all peaks were calculated with the MASAS[19] computer program by using a polynomial expansion based on natural abundances of the isotopes.

Synthesis of $[Ru_2\{\mu\text{-}O_2CC(Me)=CHEt\}_4(OCN)]_n$ (1): To a methanol solution (15 mL) of $[Ru_2\{\mu\text{-}O_2CC(Me)=CHEt\}_4]BF_4$ (0.22 g, 0.30 mmol) was added an aqueous solution of sodium cyanate (0.10 g, 1.50 mmol, 10 mL). The reaction mixture was stirred for 1 h. A brown precipitate was formed. The solid was filtered out, washed with water (4 × 20 mL) and dried under vacuum to give **1**. Yield: 161 mg (77%). $C_{25}H_{36}NO_9Ru_2$ (696.71): calcd. C 43.10, H 5.21, N 2.01; found C 42.98, H 5.11, N 2.13. Main IR data (KBr disk): 2968 (m), 2935 (m), 2876 (m), 2139 (vs), 2085 (w), 1647 (m), 1435 (v)s, 1415 (vs), 1384 (vs), 1349 (s), 1300 (w), 1258 (w), 1179 (m), 1105 (m), 1067 (w), 1036 (m), 989 (w), 906 (w), 841 (m), 786 w, 752 (m), 684 (s), 651 (w), 623 (w), 530 (s), 479 (w), 431 (w), 421 (w) cm^{-1}. $\mu_{eff.}$ (room temp.) = 3.69 μ_B. Mass spectrometric data (ESI$^+$): *m*/*z* = 656 $[Ru_2\{\mu\text{-}O_2CC(Me)=CHEt\}_4]$.

Red-brown crystals of **1** suitable for X-ray diffraction were obtained when a methanol solution of $[Ru_2\{\mu\text{-}O_2CC(Me)=CHEt\}_4]BF_4$ was layered over a water solution of NaOCN.

Synthesis of $\{[Ru_2(\mu\text{-}O_2CMe)_4][Ag(OCN)_2]\}_n$ (2): To a suspension of $[Ru_2Cl(\mu\text{-}O_2CMe)_4]$ (0.14 g, 0.30 mmol) in methanol (10 mL) was added a solution of $AgNO_3$ (0.05 g, 0.30 mmol, 5 mL). The reaction mixture was stirred for 10 min to give a solid precipitate of AgCl and a brown solution containing the species $[Ru_2(\mu\text{-}O_2CMe)_4]^+$. The precipitate was removed by filtration, and the solution was treated again with an aqueous solution of $AgNO_3$ (0.05 g, 0.30 mmol, 10 mL) and an aqueous solution of NaOCN (0.04 g, 0.60 mmol, 10 mL). The reaction mixture was stirred for one hour, in the absence of light, and gave a brown precipitate. The solid was filtered out, washed with water (2 × 20 mL) and dried under vacuum to give **2**. Yield: 110 mg (58%). $C_{10}H_{12}AgN_2O_{10}Ru_2$ (630.22): calcd. C 19.06, H 1.92, N 4.44; found C 19.20, H 1.97, N 4.42. Main IR data (KBr disk): 2937 (w), 2155 vs, 2104 (w), 1444 vs, 1398 (m), 1349 (w), 1051 (w), 694 (s), 670 (w), 662 (w), 627 (w), 615 (w) cm^{-1}. $\mu_{eff.}$ (room temp.) = 4.15 μ_B. Mass spectrometric data (ESI$^+$): *m*/*z* = 517 $[Ru_2(\mu\text{-}O_2CMe)_4(dmso)]$.

Crystals of **2** were obtained by slow diffusion of the solution containing the species $[Ru_2(\mu\text{-}O_2CMe)_4]^+$ and Ag^+ (molar ratio 1:1) over the aqueous solution of NaOCN.

Crystal Structural Data for 1: $C_{25}H_{36}NO_9Ru_2$, M_r 696.69, crystal size 0.14 × 0.18 × 0.20 mm, monoclinic, space group *P*2/*c*, a = 9.9698(8), b = 12.0247(9), c = 12.4202(9) Å, β = 98.146(2)°, V = 1473.96(19) Å^3, Z = 2, D_c = 1.570 g cm^{-3}, $F(000)$ = 706, μ = 1.072 mm^{-1}, 3559 independent reflections, R_I [$I > 2\sigma(I)$] = 0.0865, wR_2 (all data) = 0.2914.

Crystal Structural Data for 2: $C_{10}H_{12}AgN_2O_{10}Ru_2$, M_r 630.23, crystal size 0.04 × 0.04 × 0.32 mm, monoclinic, space group *P*2(1)/*n*, a = 7.3420(6), b = 8.8225(7), c = 13.1580(11) Å, β = 92.215(2)°, V = 851.67(12) Å^3, Z = 2, D_c = 2.458 g cm^{-3}, $F(000)$ = 602, μ =

2.942 mm^{-1}, 2051 independent reflections, R_I [$I > 2\sigma(I)$] = 0.0408, wR_2 (all data) = 0.1205.

Representative crystals were mounted on a Bruker Smart-CCD diffractometer with graphite monochromated Mo-K_α (λ = 0.71073 Å) radiation. Data were collected at 293(2) K over a hemisphere of the reciprocal space by a combination of three exposure sets. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 with the SHELXS and SHELXL programs.[20]

CCDC-612317 and CCDC-612318 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] a) J.-W. Ying, D. R. Sobransingh, G.-L. Xu, A. E. Kaifer, T. Ren, *Chem. Commun.* **2005**, 357–359; b) S. K. Hurst, T. Ren, *J. Organomet. Chem.* **2003**, *670*, 188–197; c) T. Ren, G.-L. Xu, *Comments Inorg. Chem.* **2002**, *23*, 355–380.

[2] a) F. A. Cotton, C. Lin, C. A. Murillo, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 4810–4813; b) F. A. Cotton, C. Lin, C. A. Murillo, *Acc. Chem. Res.* **2001**, *34*, 759–771.

[3] a) M. H. Chisholm, A. M. Macintosh, *Chem. Rev.* **2005**, *105*, 2949–2976; b) B. E. Bursten, M. H. Chisholm, J. S. D′Acchioli, *Inorg. Chem.* **2005**, *44*, 5571–5579; c) M. H. Chisholm, *Acc. Chem. Res.* **2000**, *33*, 53–61.

[4] F. A. Cotton, C. A. Murillo, R. A. Walton (Eds.), *Multiple Bonds between Metal Atoms*, 3rd ed., Springer Science and Business Media Inc., New York, **2005**.

[5] a) M. A. S. Aquino, *Coord. Chem. Rev.* **1998**, *170*, 141–202; b) M. A. S. Aquino, *Coord. Chem. Rev.* **2004**, *248*, 1025–1045.

[6] M. Mikuriya, D. Yoshioka, M. Handa, *Coord. Chem. Rev.* **2006**, *250*, 2194–2211.

[7] For example, see: a) M. C. Barral, T. Gallo, S. Herrero, R. Jiménez-Aparicio, M. R. Torres, F. A. Urbanos, *Inorg. Chem.* **2006**, *45*, 3639–3647; b) B. Liu, P. Yin, X.-Y. Yi, S. Gao, L.-M. Zheng, *Inorg. Chem.* **2006**, *45*, 4205–4213; c) E. V. Dikarev, A. S. Filatov, R. Clérac, M. A. Petrukhina, *Inorg. Chem.* **2006**, *45*, 744–751; d) M. C. Barral, S. Herrero, R. Jiménez-Aparicio, M. R. Torres, F. A. Urbanos, *Angew. Chem. Int. Ed.* **2005**, *44*, 305–307; e) P. Angaridis, F. A. Cotton, C. A. Murillo, D. Villagrán, X. Wang, *J. Am. Chem. Soc.* **2005**, *127*, 5008–5009; f) T. Ren, *Organometallics* **2005**, *24*, 4854–4870; g) W.-Z. Chen, T. Ren, *Organometallics* **2005**, *24*, 2660–2669.

[8] a) M. C. Barral, R. Jiménez-Aparicio, J. L. Priego, E. C. Royer, F. A. Urbanos, U. Amador, *J. Chem. Soc., Dalton Trans.* **1997**, 863–868; b) M. Mukaida, T. Nomura, T. Ishimori, *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2143–2147.

[9] For example, see: a) T. E. Vos, J. S. Miller, *Angew. Chem. Int. Ed.* **2005**, *44*, 2416–2419; b) T. Sugiura, K. Ota, M. Ebihara, T. Kawamura, *C. R. Chim.* **2005**, *8*, 1760–1765; c) O. Kahn, *Acc. Chem. Res.* **2000**, *33*, 647–657.

[10] M. C. Barral, R. Jiménez-Aparicio, D. Pérez-Quintanilla, E. Pinilla, J. L. Priego, E. C. Royer, F. A. Urbanos, *Polyhedron* **1998**, *18*, 371–376.

[11] G. Arribas, M. C. Barral, R. González-Prieto, R. Jiménez-Aparicio, J. L. Priego, M. R. Torres, F. A. Urbanos, *Inorg. Chem.* **2005**, *44*, 5770–5777.

[12] For example, see: a) Effendy, C. Di Nicola, C. Pettinari, A. Pizzabiocca, B. W. Skelton, N. Somers, A. H. White, *Inorg. Chim. Acta* **2006**, *359*, 64–80 and references cited therein; b) Effendy, C. Di Nicola, M. Fianchini, C. Pettinari, B. W. Skelton, N. Somers, A. H. White, *Inorg. Chim. Acta* **2005**, *358*, 763–795; c) G. A. Bowmaker, Effendy, P. C. Junk, A. H. White, *J. Chem. Soc., Dalton Trans.* **1998**, 2131–2138 and references cited therein.

[13] K. Aarflot, K. Ase, *Acta Chem. Scand. Ser. A* **1974**, *28*, 137–144.

[14] J. G. Norman, G. E. Renzoni, D. A. Case, *J. Am. Chem. Soc.* **1979**, *101*, 5256–5267.

[15] F. D. Cukiernik, D. Luneau, J. C. Marchon, P. Maldivi, *Inorg. Chem.* **1998**, *37*, 3698–3704.

[16] R. Jiménez-Aparicio, F. A. Urbanos, J. M. Arrieta, *Inorg. Chem.* **2001**, *40*, 613–619.

[17] Y. Shi, G. T. Yee, G. Wuang, T. Ren, *J. Am. Chem. Soc.* **2004**, *126*, 10552–10553.

[18] R. W. Michell, A. Spencer, G. Wilkinson, *J. Chem. Soc., Dalton Trans.* **1973**, 846–854.

[19] F. A. Urbanos, *MASAS*, version 3.1, University Complutense of Madrid, Madrid, Spain, **2002**.

[20] a) G. M. Sheldrick, *SHELXS-97*, University of Göttingen, Göttingen, Germany, **1997**; b) G. M. Sheldrick, *SHELXL-97*, University of Göttingen, Göttingen, Germany, **1997**.

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