Available online at www.sciencedirect.com
SCIENCE DIRECT®

ELSEVIER

Journal of Organometallic Chemistry 689 (2004) 2641–2645

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

Heterobimetallic complexes as oxygen donor bidentate ligands: synthesis of early–late trinuclear complexes

Rosa Fandos [a,*], Antonio Otero [b,*], Ana Rodríguez [c], María José Ruiz [a], Pilar Terreros [d]

[a] *Departamento de Química Inorgánica, Orgánica y Bioquímica, Universidad de Castilla-La Mancha, Facultad de Ciencias del Medio Ambiente. Avd. Carlos III, s/n, 45071 Toledo, Spain*
[b] *Departamento de Química Inorgánica, Orgánica y Bioquímica, Universidad de Castilla-La Mancha, Facultad de Químicas, Campus de Ciudad Real, Avd. Camilo José Cela, 10, 13071 Ciudad Real, Spain*
[c] *Departamento de Química Inorgánica, Orgánica y Bioquímica, Universidad de Castilla-La Mancha, ETS Ingenieros Industriales, Campus de Ciudad Real, Avd. Camilo José Cela, 3, 13071 Ciudad Real, Spain*
[d] *Instituto de Catálisis y Petroleoquímica, CSIC, Cantoblanco, 28049 Madrid, Spain*

Received 29 March 2004; accepted 20 May 2004
Available online 2 July 2004

Abstract

The early–late heterometallic complexes [TiCp*((OCH$_2$)$_2$Py)(μ-O)M(COD)] (M = Rh, Ir) behave as four-electron donor ligands yielding the polynuclear cationic complexes [TiCp*(OCH$_2$)$_2$ Py(μ-O){M(COD)}$_2$]OTf (M = Rh (**1**), Ir (**2**)). The molecular structure of complex **1** has been established through an X-ray diffraction study.

Keywords: Alkoxide ligands; Heterometallic complexes; Rhodium; Titania

1. Introduction

The chemistry of early–late heteropolynuclear complexes has been extensively investigated in recent years on account of their relevance to bioinorganic systems and their potentials in homogeneous catalysis [1]. Among them, those with oxygen acting as a bridging ligand between an early transition metal and a late one are of relevance in part because such compounds can be considered as model compounds of late transition metals based catalysts supported on early metal oxides, such as titania, and therefore can provide an insight into the into the chemistry taking place in the active site, at the interface between a metal and its oxide support [2,3]. On the other hand, it is very important to establish a relation between the stability of the catalyst and its structure to avoid the leaching which can also alter its performance [4]. Besides, immobilization of organometallic compounds on solid surfaces such as oxides, zeolites, or metals is a field of growing interest in organometallic chemistry [5]. This subject is attracting the attention of chemists on account of the highly active surface species involved in the heterogeneous catalysis. However, as in the case of the classical heterogeneous catalysts, the nature of the bonding, and the mechanism by which the metallic precursor behaves is not always fully understood. Therefore, obtaining three-dimensional molecular model compounds is desirable in order to identify more exactly the species present on a supported surface and understand the bonding between the metal and oxide surfaces and how these properties are related to the catalytic activity [6].

We have recently reported the synthesis of heterometallic complexes such as [TiCp*((OCH$_2$)$_2$Py)(μ-O)M-

---

[*] Corresponding authors. Tel.: +34-92-629-5326; fax: +34-92-629-5318.
E-mail address: antonio.otero@uclm.es (A. Otero).

0022-328X/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2004.05.025

(COD)] (M = Rh, Ir) [7] which can be considered as models of a single M atom bound to TiO_2 and we present here their reactivity as bidentate four-electron donors ligands to yield trinuclear complexes in which two M atoms are closed together bound to the oxide.

2. Results and discussion

The heterometallic complexes [TiCp*($(OCH_2)_2$Py)-(μ-O)M(COD)] (M = Rh, Ir) react with the cationic derivatives [M(COD)$(THF)_2$]OTf (generated "in situ" by reaction of [M(μ-Cl)(COD)$]_2$ with AgOTf in THF) at room temperature in an 1:1 ratio to yield complexes **1** (Rh) and **2** (Ir) (see Scheme 1). Complex **1** is stable in the solid state or in solution while compound **2** decomposes in a few hours, at room temperature, in $CDCl_3$ solution.

Complexes **1** and **2** have been characterized by the usual spectroscopic techniques. The NMR data of both complexes indicate that in solution the rhodium (**1**) or iridium (**2**) metal centers are in the same chemical environment and in agreement with that the methylene groups in the alkoxide ligand are also equivalent. As an example, the ^{1}H NMR of **2** shows four multiplet signals at 1.46, 2.21, 3.87 and 4.08 ppm corresponding to the methylene and to the olefinic protons of the COD moiety. The methylene protons of the dialkoxide ligand give rise to two doublet signals centered at 5.19 and 5.90 ppm. On the other hand, aromatic protons are located at 7.53 and 8.09 ppm appearing as multiplet signals.

The ^{13}C NMR spectrum is also consistent with the proposal of an equivalent coordination environment for both iridium atoms and shows two singlet signals at 13.3 and 143.7 ppm corresponding to the Cp* ligand. The absorption due to the methylene groups of the COD appear at 31.9 and 32.1 while the olefinic carbon atoms give rise to two signals at 60.3 and 62.4 ppm. On the other hand, the alkoxide moiety can be seen through a singlet at 78.6 ppm corresponding to the methylene carbon atoms and three other signals at 120.1, 127.9 and 163.1 assigned to the aromatic carbon atoms. According to the proposed geometry the COD ligand should give rise to four signals corresponding to the olefinic protons while only two are observed. These data point out to a fluxional process.

An ^{1}H VTNMR experiment carried out in $CDCl_3$ confirms a fluxional behavior. At 243 K one of the two signals observed at room temperature corresponding to the COD ligand (4.00 ppm) reaches the coalescence. At 223 K the spectrum shows three broad signals at 4.22 (2 H), 3.82 (4 H) and 3.78 (2 H) ppm corresponding to the olefinic protons of the cyclooctadiene

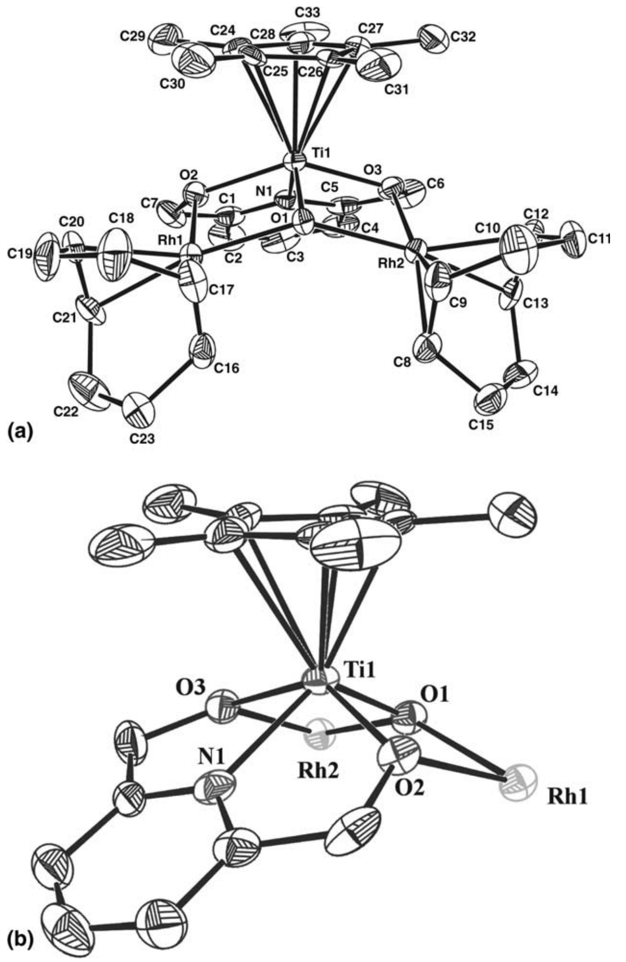
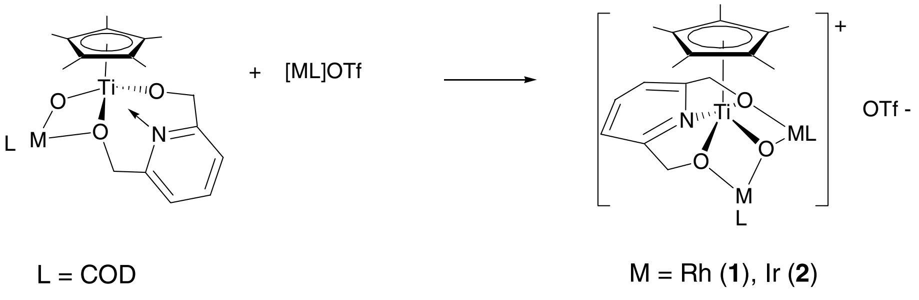


Fig. 1. (a) Molecular structure of **1** showing thermal ellipsoids and the labeling scheme. (b) Main frame of the molecular structure of complex **1**.



Scheme 1.

ligand. Unfortunately the low exchange limit could not be reached under these conditions.

Complex **1** has also been characterized by an X-ray diffraction study. An ORTEP drawing of one of the two independent molecules found in the structural study is shown in Fig. 1, and some selected bond distances and angles are summarized in Table 1.

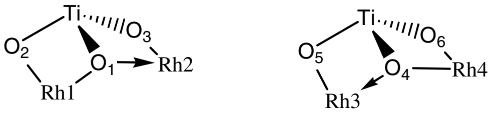
The structure is built up of trimetallic ($TiRh_2$) cationic units. The geometry around the titanium atom is that of an pseudo-square pyramid while around the rhodium atoms is roughly planar. The mid points of the two C=C (COD) bonds, the two oxygen atoms bound to the Rh(1) and the Rh(2) centers are coplanar within 0.01 and 0.05 Å, respectively.

Distance from titanium to the plane containing the cyclopentadienyl ring (2.077 Å) is normal for titanium complexes [8]. Ti(1)–O(2) and Ti(1)–O(3) distances are 1.991 (6) and 1.988 (6) Å which are within the range found in other titanium complexes with bridging alkoxide ligands [9]. On the other hand, Ti(1)–O(1) bond distance is shorter (1.794 (6) Å) [10] as it is expected for bridging oxide ligands.

The intermetallic Rh(1)–Ti(1) and Rh(2)–Ti(1) distances are 2.971 (2) and 2.984 (2) Å, respectively. The Ti–Rh separation is in the range of that found in some previously reported heterometallic complexes for which a metal–metal interaction has been proposed [11].

Table 1
Bond lengths (Å) and angles (°) for **1**

Bond lengths		Angles	
Rh(1)–Ti(1)	2.972(2)	C(17)–Rh(1)–C(16)	38.5(4)
Rh(1)–C(16)	2.12(1)	C(21)–Rh(1)–C(20)	39.0(4)
Rh(1)–C(17)	2.08(1)	O(1)–Rh(1)–O(2)	78.2(2)
Rh(1)–C(20)	2.10(1)	C(9)–Rh(2)–C(8)	38.7(4)
Rh(1)–C(21)	2.099(9)	C(13)–Rh(2)–C(12)	38.4(4)
Rh(1)–O(1)	2.109(5)	O(3)–Rh(2)–O(1)	77.8(2)
Rh(1)–O(2)	2.119(6)	O(1)–Ti(1)–O(3)	88.8(3)
Rh(2)–O(1)	2.126(5)	O(1)–Ti(1)–O(2)	89.4(2)
Rh(2)–O(3)	2.092(6)	O(3)–Ti(1)–O(2)	139.2(3)
Rh(2)–C(8)	2.09(1)	O(1)–Ti(1)–N(1)	121.5(3)
Rh(2)–C(9)	2.09(1)	O(3)–Ti(1)–N(1)	72.7(3)
Rh(2)–C(12)	2.101(9)	O(2)–Ti(1)–N(1)	73.8(3)
Rh(2)–C(13)	2.095(9)	Rh(1)–Ti(1)–Rh(2)	86.22(5)
Rh(2)–Ti(1)	2.984(2)	Ti(1)–O(1)–Rh(1)	98.9(2)
Ti(1)–O(1)	1.794(6)	Ti(1)–O(1)–Rh(2)	98.8(3)
Ti(1)–O(2)	1.991(6)	Rh(1)–O(1)–Rh(2)	148.0(3)
Ti(1)–O(3)	1.988(6)	Ti(1)–O(2)–Rh(1)	92.6(2)
Ti(1)–N(1)	2.137(8)	Ti(1)–O(3)–Rh(2)	94.0(3)
Ti(1)–C(24)	2.40(1)		
Ti(1)–C(25)	2.35(1)		
Ti(1)–C(26)	2.332(9)		
Ti(1)–C(27)	2.44(1)		
Ti(1)–C(28)	2.45(1)		
O(2)–C(7)	1.42(1)		
O(3)–C(6)	1.41(1)		
N(1)–C(1)	1.36(1)		
N(1)–C(5)	1.32(1)		



Scheme 2.

The two independent molecules in the unit cell could be account for considering the bonding modes proposed in Scheme 2.

3. Conclusion

In conclusion, we report in this paper the ability of the heterobimetallic complexes $[TiCp^*((OCH_2)_2Py)(\mu\text{-}O)\{M(COD)\}_2]OTf$ (M = Rh, Ir) to behave as bidentate ligands yielding early–late trinuclear complexes. An study of the possible coordination of the new ligands to different metals is under way.

4. Experimental

The preparation and handling of described compounds was performed with rigorous exclusion of air and moisture under nitrogen atmosphere using standard vacuum line and Schlenk techniques. All solvents were dried and distilled under a nitrogen atmosphere.

The following reagents were prepared by literature procedures: $[Rh(\mu\text{-}Cl)(COD)]_2$ [12] and $[Ir(\mu\text{-}Cl)(COD)]_2$ [13] The commercially available compounds, HOTf were used as received from Aldrich.

^1H and ^{13}C NMR spectra were recorded on 200 Mercury Varian Fourier Transform spectrometer. Trace amounts of protonated solvents were used as references, and chemical shifts are reported in units of parts per million relative to $SiMe_4$.

IR spectra were recorded in the region 4000–400 cm^{-1} with a Nicolet Magna-IR 550 spectrophotometer.

4.1. Synthesis of $[TiCp^*((OCH_2)_2Py)(\mu\text{-}O)\{Rh(COD)\}_2]OTf$ (*1*)

To a mixture of $[RhCl(COD)]_2$ (40 mg, 0.081 mmol) and AgOTf (42 mg, 0.163 mmol) was added THF (5 mL), at room temperature, and the mixture was stirred during 30 min. After that, $[TiCp^*((OCH_2)_2Py)(\mu_2\text{-}O)Rh(COD)]$ was added (89 mg, 0.162 mmol) and the suspension was stirred, at room temperature, for 1 h. After filtration the solvent was removed under vacuum and the residue washed with 5 mL of pentane to yield 88 mg (60%) of complex **1**. IR (cm^{-1}): 1609 (m), 1582 (w), 1476 (vs), 1452 (s), 1272 (vs), 1214 (vs), 1151 (vs), 1056 (m), 1036 (s), 783 (m), 636 (s), 515 (s). ^1H NMR (200 MHz, $CDCl_3$, rt): $\delta = 1.72$ (m, 8 H, COD), 2.16

(s, 15 H, Cp*), 2.46 (m, 8 H, COD), 3.87 (m, 4 H, COD), 4.00 (m, 4 H, COD), 4.98 (d, 2 H, $^2J_{H–H}=17.59$ Hz, OCH_2), 5.58 (d, 2 H, $^2J_{H–H}=17.59$ Hz, OCH_2), 7.44 (m, 2 H, Ar), 8.00 (m, 1 H, Ar). ^{13}C{^{1}H} NMR: 13.0 (s, Cp*), 31.1 (s, COD), 31.2 (s, COD), 76.5 (d, $^1J_{Rh–C}=14.86$ Hz, COD), 77.2 (s, CH$_2$), 79.0 (d, $^1J_{Rh–C}=14.86$ Hz, COD), 119.5 (s, Ar), 125.3 (s, Ar), 142.9 (s, Cp*), 163.4 (s, Ar$_{ipso}$). Anal. Calc. for $C_{34}H_{46}F_3NO_6SRh_2Ti$: C, 45.0; H, 5.1; N, 1.5. Found: C, 44.8; H, 5.0; N, 1.5%.

4.2. Synthesis of [TiCp((OCH$_2$)$_2$Py)(μ-O){Ir(COD)}$_2$]OTf (**2**)*

To a mixture of [IrCl(COD)]$_2$ (129 mg, 0.192 mmol) and AgOTf (99 mg, 0.385 mmol) was added THF (7 mL) at room temperature, and the mixture was stirred during 15 min. After that, [TiCp*((OCH$_2$)$_2$Py)(μ$_2$-O)Ir(COD)] (245 mg, 0.384 mmol) was added and the suspension was stirred, at room temperature for 1 h. After filtration the solvent was removed under vacuum and the residue washed with 8 mL of pentane to yield 251 mg (60%) of complex **2**. IR (cm^{-1}): 1603 (m), 1582 (w), 1476 (vs), 1452 (s), 1272 (vs), 1214 (vs), 1146 (vs), 1040 (s), 1025 (s), 794 (m), 725 (s), 678 (s), 636 (s), 541 (s). ^{1}H NMR (200 MHz, CDCl$_3$, rt): $\delta=1.46$ (m, 8 H, COD), 2.11 (s, 15 H, Cp*), 2.21 (m, 8 H, COD), 3.87 (m, 4 H, COD), 4.08 (m, 4 H, COD), 5.19 (d, 2 H, $^2J_{H–H}=17.23$ Hz, OCH_2), 5.90 (d, 2 H, $^2J_{H–H}=17.23$ Hz, OCH_2), 7.53 (m, 2 H, Ar), 8.09 (m, 1 H, Ar). ^{13}C{^{1}H} NMR: 13.3 (s, Cp*), 31.9 (s, COD), 32.1 (s, COD), 60.3 (s, COD), 62.4 (s, COD), 78.6 (s, CH$_2$), 120.1 (s, Ar), 127.9 (s, Ar), 143.7 (s, Cp*), 163.1 (s, Ar$_{ipso}$). Anal. Calc. for $C_{34}H_{46}F_3NO_6SIr_2Ti$: C, 37.7; H, 4.3; N, 1.3. Found: C, 37.7; H, 4.1; N, 1.2%.

*4.3. X-ray structure analysis of **1***

A yellow crystal of approximate dimensions of 0.3×0.2×0.2 mm was mounted in a glass capillary. Crystallographic data are listed in Table 2.

Intensity data were collected on a NONIUS-MACH3 diffractometer equipped with a graphite monochromated Mo Kα radiation ($\lambda=0.71073$ Å) using an $\omega/2\theta$ scan technique to a maximum value of 56°. Crystal are monoclinic of space group $P2_1/n$ with two molecules per asymmetric unit. Data were corrected in the usual fashion for Lorentz and polarization effects and empirical absorption correction was not necessary. The structure was solved using directs methods [14]. Refinement on F^2 was carried out by full-matrix least-squares techniques [15]. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were include in calculated position and were refined isotropically. Refinement (16,957 reflections, 875 parameters) converged to give the following values: $R_1=0.0669$, $wR_2=0.0989$, GOF = 0.929 for 6243 reflections with $I>2\sigma I$. Maximum and minimum residual electron densities, 0.652 and −0.860 eÅ^{-3}.

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

Empirical formula	$C_{33}H_{46}NO_3Rh_2Ti \cdot CF_3SO_3$
Formula weight	907.50
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/n$
Unit cell dimensions	
a	27.754(4) Å
b	13.769(2) Å,
β	97.94(3)°
c	18.754(4) Å
V	7098(2) Å^3
Z, calculated density	8, 1.698 g/cm^3
Absorption coefficient	12.58 cm^{-1}
$F_{(000)}$	3680
Crystal size	0.3×0.2×0.2 mm
Limiting indices	$-36 \leq h \leq 36$, $0 \leq k \leq 18$, $0 \leq l \leq 24$
Reflections collected/unique	17,463/16,957 [$R_{int}=0.1070$]
Data/restraints/parameters	16,957/0/875
Goodness-of-fit on F^2	0.929
Final *R* indices [$I>2\sigma(I)$]	$R_1=0.0669$, $wR_2=0.0989$
Largest difference peak and hole	0.652 and −0.860 eÅ^{-3}

Acknowledgements

This work was supported by the Ministerio de Ciencia y Tecnología, Spain (Grant Nos. BQU2002-04638-C02-02 and MAT2001-2215-C03-01) and the Junta de Comunidades de Castilla-La Mancha (Grant Nos. PAC-02-003 and GC-02-010).

Appendix A. Supplementary material

Crystallographic data for the structural analysis of **1** have been deposited with the Cambridge Crystallographic Data Centre, CCDC-214312. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.jorganchem.2004.05.025.

References

[1] N. Wheatley, P. Kalck, Chem. Rev. 99 (1999) 3379.
[2] (a) R. Fandos, C. Hernández, A. Otero, A. Rodríguez, M.J. Ruiz, P. Terreros, Organometallics 18 (1999) 2718;
(b) R. Fandos, J.L. Fierro, M.M. Kubicki, A. Otero, P. Terreros, M.A. Vivar-Cerrato, Organometallics 14 (1995) 2162;

(c) D. Selent, P. Claus, J. Pckardt, J. Organomet. Chem. 468 (1994) 131;

(d) M.S. Rau, C.M. Kretz, G.L. Geoffroy, A.L. Rheingold, B.S. Haggerty, Organometallics 13 (1994) 1624 and references therein;

(e) R. Xi, B. Wang, M. Abe, Y. Ozawa, K. Isobe, Chem. Lett. (1994) 1177;

(f) R. Xi, B. Wang, M. Abe, Y. Ozawa, K. Isobe, Chem. Lett. (1994) 323;

(g) K. Isobe, A. Yagasaki, Acc. Chem. Res. 26 (1993) 524.

[3] S.J. Tauster, Acc. Chem. Res. 20 (1987) 389.

[4] E.R. Hartley, Supported Metal Complexes D, Reidel, Dordrecht, Holland, 1985.

[5] (a) A.O. Bouth, G.L. Rice, S.L. Scott, J. Am. Chem. Soc. 121 (1999) 7201;

(b) P. Dufour, S.L. Scott, C.C. Santini, F. Lefebvre, J.-M. Basset, Inorg. Chem. 33 (1994) 2509;

(c) C. Copéret, M. Chabanas, R.P. Saint-Arroman, J.M. Basset, Angew. Chem. Int. Ed. Engl. 42 (2003) 156.

[6] A.I. Gouzyr, H. Wessel, C.E. Barnes, H.W. Roesky, M. Teichert, I. Usón, Inorg. Chem. 36 (1997) 3392.

[7] R. Fandos, C. Hernández, A. Otero, A. Rodríguez, M.J. Ruiz, P. Terreros, Chem. Eur. J. 9 (2003) 671.

[8] M. Mena, M.A. Pellinghelli, P. Royo, R. Serrano, A. Tiripicchio, J. Chem. Soc. Chem. Commun. (1986) 1118.

[9] V.W. Day, T.A. Eberspacher, J. Hao, W.G. Klemperer, B. Zhong, Inorg. Chem. 43 (1995) 3549.

[10] (a) F. Bottomley, I.J.B. Lin, P.S. White, J. Am. Chem. Soc. 103 (1981) 704;

(b) J. Okuda, E. Herdtweck, Inorg. Chem. 30 (1991) 1516;

(c) T.J. Clark, T.A. Nile, D. McPhail, A.T. McPhail, Polyhedron 8 (1989) 1804;

(d) P. Gómez-Sal, A.M. Irigoyen, M. Mena, M. Monge, C. Yélamos, J. Organomet. Chem. 494 (1995) C19.

[11] (a) J.W. Park, L.M. Henling, W.P. Schaefer, R.H. Grubbs, Organometallics 10 (1991) 171;

(b) T.T. Nadasdi, D.W. Stephan, Inorg. Chem. 32 (1994) 1532.

[12] G. Giordano, R.H. Crabtree, Inorg. Synth. 19 (1979) 218.

[13] J.L. Herde, J.C. Lambert, C.V. Senoff, Inorg. Synth. 15 (1974) 18.

[14] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, J. Appl. Cryst. 32 (1999) 115–119.

[15] Programs for Crystal Structure Analysis (Release 97-2). Sheldrick, G.M., Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.