Bull. Chem. Soc. Ethiop. **2007**, 21(1), 75-81. ISSN 1011-3924
Printed in Ethiopia

SYNTHESIS AND CRYSTAL STRUCTURE OF AN OXORHENIUM(V) COMPLEX CONTAINING A TRIDENTATE IMIDAZOLE LIGAND

Zenixole R. Tshentu[1*], Thomas I.A. Gerber[1] and Peter Mayer[2]

[1]Department of Chemistry, Nelson Mandela Metropolitan University, P.O. Box 77000, Port Elizabeth 6031, South Africa
[2]Department of Chemistry, Ludwig-Maximilians University, D-81377 München, Germany

(Received February 28, 2006; March 31, 2006)

ABSTRACT. The reaction of equimolar amounts of (n-Bu_4N)[$ReOCl_4$] and 2-(1-ethanolthiomethyl)-1-methylimidazole (Htmi) in acetonitrile yielded *cis*-[$ReOCl_2$(tmi)]. An X-ray diffraction study shows that tmi^- coordinates as a uninegative N,S,O-tridentate ligand to give distorted octahedral geometry around the rhenium(V) ion. The three donor atoms occupy a triangular face in an octahedron, with the alcoholate oxygen coordinated *trans* to the oxo group.

KEY WORDS: Oxorhenium(V), N,S,O-tridentate, Imidazole

INTRODUCTION

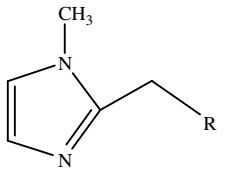
There is significant contemporary interest in the coordination chemistry of rhenium because the radionuclides ^{186}Re and ^{188}Re are β-emitters with properties suitable for use in therapeutic nuclear medicine [1, 2].

The challenge for inorganic chemists is to design low molecular weight, biologically active rhenium complexes that can selectively bind to tumour cells to deliver radiation *in situ* to the cancerous tissue. Therefore, an intensive study of the coordination chemistry of rhenium becomes a priority in order to advance radiopharmaceutical development.

We have become interested in the study of rhenium complexes with multidentate ligands containing the imidazole group, mainly due to the importance of the latter group in biological processes [3]. For example, the imidazole moiety plays an important role in biological systems as a part of the histidyl residue in peptides and proteins [3-6]. Moreover, the imidazole derivatives show a diverse range of pharmacological activity such as antibacterial, antifungal, as well as antitumoural effects [7].

We have earlier found that the reaction of the neutral bidentate N,S-donor ligand 2-(1-ethylthiomethyl)-1-methylimidazole (etmi) with *trans*-[$ReOCl_3(PPh_3)_2$] or (n-Bu_4N)[$ReOCl_4$] in air yields an oxo-bridged dinuclear complex [(μ-O){$ReOCl_2$(etmi)}$_2$] [8]. Under anaerobic conditions, the reaction of etmi with *trans*-[$ReOCl_3(PPh_3)_2$] in ethanol led to the isolation of the cationic complex [ReOCl(OEt)(etmi)(PPh_3)]X (X = ReO_4, PF_6) [9]. These products reflect the propensity for anionic O-donors to occupy the position *trans* to the oxo group. We have therefore introduced an extension of the bidentate ligand (etmi) to include a terminal aliphatic O-donor in the tridentate ligand 2-(1-ethanolthiomethyl)-1-methylimidazole (Htmi). Its reaction with (n-Bu_4N)[$ReOCl_4$] in acetonitrile led to the isolation of a neutral monomer *cis*-[$ReOCl_2$(tmi)] (**1**), in which tmi^- is coordinated as a monoanionic tridentate ligand *via* the neutral nitrogen, sulfur and deprotonated alcohol oxygen.

*Corresponding author. E-mail: zenixole.tshentu@nmmu.ac.za



R = SCH_2CH_3 (etmi)
R = SCH_2CH_2OH (Htmi)
R = $NHCH_2CH_2OH$ (Hami)

EXPERIMENTAL

Reagents

(n-Bu_4N)[$ReOCl_4$] and the salt 2-chloromethyl-1-methylimidazole hydrochloride were prepared by literature methods [10, 11]. Solvents were purified and dried before use. Laboratory chemicals were of reagent grade and were used without further purification.

Instrumentation

IR spectra were recorded for samples in NaCl cells (Htmi) and KBr pellet (**1**) on a Nicolet 20 DXC FTIR spectrophotometer. ^{1}H HMR spectra were recorded at 300 MHz on a Bruker AMX-300 spectrometer. All chemical shifts are relative to TMS, with DMSO-d_6 as a solvent. The optical spectrum was obtained using a Perkin-Elmer 330 UV-Vis spectrophotometer. Conductivity measurements were made with 10^{-3} M solutions in DMF at 293 K on a Philips PW9509 digital conductometer. The electronic spectrum and conductivity measurement (in units $cm^2ohm^{-1}mol^{-1}$) were obtained from samples in DMF, and the spectroscopic data are given as λ_{max} (in nm) with extinction coefficients (in units $M^{-1}cm^{-1}$) in parentheses. Elemental analyses were carried out by the Department of Chemistry at the University of the Western Cape in Cape Town.

Synthesis of 2-(1-ethanolthiomethyl)-1-methylimidazole (Htmi)

2-Chloromethyl-1-methylimidazole hydrochloride (5.00 g, 30 mmol) was suspended in 20 mL ethanol, and K_2CO_3 (6.20 g, 45 mmol) was added. To this mixture was added a solution of 2-mercaptoethanol (2.34 g, 30 mmol), dissolved in 20 mL ethanol, and the mixture was heated under reflux for an hour and then stirred overnight. A white precipitate (KCl) was filtered off and the solvent ethanol was then removed under reduced pressure, to leave brown oil. The oil was taken up in 50 mL of chloroform, more KCl was filtered off, and the solution was dried with anhydrous sodium sulfate. On removal of the chloroform by rotary evaporation, yellow oil was obtained which was distilled under vacuum. Its boiling point was 167 ºC at 5 mTorr. Yield = 78 %. Anal. calcd. for $C_7H_{12}N_2OS$: C, 48.80; H, 7.02; N, 16.27; S, 18.62. Found: C, 48.48; H, 6.91; N, 15.93; S, 18.47. ^{1}H NMR (ppm): 2.68 (2H, t, SCH_2); 3.65 (3H, s, NCH_3); 3.80 (2H, t, CH_2O); 3.88 (2H, s, CH_2S); 6.84 and 6.90 (2H, 2xd, Ar-H).

Synthesis of [$ReOCl_2$(tmi)] (**1**)

(n-Bu_4N)[$ReOCl_4$] (100 mg, 170 µmol) was dissolved in 10 mL of acetonitrile, and an equimolar amount of Htmi (29 mg), in 5 mL acetonitrile, was added dropwise with stirring at room temperature. The solution was then heated to reflux for 1 hour, and a violet-purple solution was obtained. It was cooled to room temperature, and placed in a desiccator. After several hours, violet crystals suitable for X-ray analysis were obtained. Yield = 85 %, m.p. =

258 °C. Anal. calcd. for $C_7H_{11}N_2O_2SCl_2Re$: C, 18.92; H, 2.50; N, 6.31. Found: C, 18.81; H, 2.55; N, 6.48. IR (cm^{-1}): ν(C=N) 1632, 1564; ν(C=C) 1495; ν(H_2C-O) 1172; ν(Re=O) 945; ν(Re-N) 470; ν(Re-Cl) 320, 318; ν(Re-S) 266. ^{1}H NMR (ppm): 2.92 (2H, t, C(5)H_2); 3.07 (2H, t, C(6)H_2); 3.89 (3H, s, C(7)H_3); 4.45 (2H, s, C(4)H_2); 7.57 and 7.72 (2H, 2xd, Ar-H(1)(2)). UV-Vis (λ_{max}, nm/ε, $M^{-1}cm^{-1}$): 310 (18800), 383 (1600), 555 (700). Conductivity (10^{-3} M) = 26.7.

X-ray crystallography

An X-ray diffraction study on crystals of [$ReOCl_2$(tmi)] (**1**) was performed at 200(2) K using a Nonius Kappa CCD diffractometer with graphite-monochromated Mo K_α radiation (λ = 0.71073 Å). The molecular structure representation, along with the atom-numbering scheme, is shown in Figure 1. Details of the crystal data are given in Table 1, with selected bond lengths and angles in Table 2. The structure was solved by direct methods. Non-hydrogen atoms were refined with anisotropic displacement parameters. Each H atom was placed in a calculated position and refined using a riding model. Structural refinements were made by the full-matrix least-squares method on F^2 using the program SHELXL-97 [12].

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

Property	[$ReOCl_2$(tmi)]
Chemical formula	$C_7H_{11}N_2O_2SCl_2Re$
Formula weight	444.35
Temperature, K	200(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions (Å,°)	a = 6.6513(5), b = 14.1633(9), c = 12.6066(8) β = 94.512(5)
Crystal size (mm)	0.12 x 0.20 x 0.33
Volume ($Å^3$)	1183.92(14)
Z	4
Density (calc.) (Mg/m^3)	2.493
Absorption coefficient (mm^{-1})	10.872
θ range for data collection (°)	4.3-27.5
Index ranges	$-8 \le h \le 8$, $-13 \le k \le 18$, $-16 \le \ell \le 14$
Reflections measured	6699
Independent/observed reflections	2729 (R = 0.0720)/2510 [$I>2\sigma(I)$]
Data/restraints/parameters	2729/0/136
Goodness of fit on F^2	1.09
Final R indices [$I>2\sigma(I)$]	R = 0.0238, $wR2$ = 0.0539
Largest diff. peak and hole ($e/Å^3$)	2.22, -1.40

RESULTS AND DISCUSSION

Synthesis

The reaction of equimolar amounts of 2-(1-ethanolthiomethyl)-1-methylimidazole (Htmi) with (n-Bu_4N)[$ReOCl_4$] in acetonitrile led to the isolation of the neutral complex *cis*-[$ReOCl_2$(tmi)], as described by the following equation:

(n-Bu_4N)[$ReOCl_4$] + Htmi → [$ReOCl_2$(tmi)] + n-Bu_4NCl + HCl

Due to the viscosity of the oily Htmi ligand, acetonitrile was found to be the only solvent suitable as a reaction medium, and X-ray quality crystals were deposited from the mother liquor.

Complex **1** is diamagnetic (formally d^2) and a non-electrolyte in DMF [13]. It is weakly soluble, but stable, in polar solvents such as acetonitrile, DMSO and DMF.

Spectral analysis

In the infrared spectrum of complex **1**, the Re=O stretching frequency appears as a sharp strong band at 945 cm^{-1}, which falls in the region of 940-970 cm^{-1} that is normally observed for six-coordinate rhenium(V) complexes containing a hard alkoxy donor atom *trans* to the Re=O moiety [14]. Coordination of the imidazolyl nitrogen is indicated by the shift of ν(C=N) from around 1670 cm^{-1} in the free ligand (Htmi) to 1632 cm^{-1} in the complex. This coordination-induced frequency change is typical for ring systems of this type [15, 16]. A band of weak intensity at 470 cm^{-1} is ascribed to ν(Re-N), and a strong band at 266 cm^{-1}, assigned to ν(Re-S), signifies the coordination of the sulfur donor atom of Htmi. The coordination of the deprotonated alkoxy oxygen of Htmi in the complex is reflected in ν(H_2C-O) at 1172 cm^{-1}.

The ^{1}H NMR spectrum of (**1**) shows sharp, well-resolved peaks and there are no detectable paramagnetic shifts or line broadening of the signals. The protons on the aliphatic substituent of tmi^- in the complex give rise to the expected singlet-triplet-triplet pattern, with a slight downfield shift of the C(4)H_2 and the C(5)H_2 proton signals, while the C(6)H_2 proton signals show a significant upfield shift from 3.80 ppm in the free ligand to 3.07 ppm in the complex. The ring protons also show two doublets as expected, and these signals are shifted markedly downfield in the complex relative to the free ligand, from 6.84 and 6.90 ppm to 7.57 and 7.72 ppm, respectively.

Description of the structure

The structure of **1** is shown in Figure 1. The packing in the unit cell (Figure 2) shows discrete, monomeric and neutral oxorhenium(V) units [$ReOCl_2$(ami)], packed with no intermolecular contacts shorter than the van der Waals radii sum. The complex crystallises in a monoclinic $P2_1/n$ space group with four molecules per unit cell. The coordination geometry around the rhenium is highly distorted octahedral; the nitrogen and sulfur atoms from the tridentate uninegative N(1),S,O(1)-donor lie on the equatorial plane, along with the two *cis*-chlorides, while the alcoholate O(1) atom is *trans* to the O(2)-oxo atom.

The rhenium atom is displaced by 0.152 Å from the least squares N(1)SCl(1)Cl(2) plane towards the oxo oxygen atom. This displacement is the result of the non-orthogonal angles O(2)-Re-Cl(1) = 92.6(1)°, O(2)-Re-N(1) = 92.3(2)°, O(2)-Re-S = 86.6(1)° and O(2)-Re-Cl(2) = 102.9(1)°. The distortion mainly results in a non-linear O(1)-Re-O(2) axis of 165.8(1)°, accomplished by Cl(1)-Re-N(1) and Cl(2)-Re-S angles of 173.5(1)° and 169.6(1)°, respectively. The two 'bite' angles of tmi^-, i.e. N(1)-Re-S = 81.8(1)° and S-Re-O(1) = 79.3(1)°, contribute considerably to this distortion. The Re atom is +1.07(2) Å from the Cl(1)Cl(2)O(2) plane and -1.36(2) Å from the N(1)SO(1) one, the angle between the two triangular faces being 7.9(1)°.

The imidazole ring is planar, as can be expected from an aromatic system, with torsion angles C(3)-N(2)-C(2)-C(1) = 0.2(5)° and N(1)-C(1)-C(2)-N(2) = -0.1(5)°, for example. The C(1)-C(2) bond is a double bond at 1.356(7) Å, and the N(1)-C(1) and N(2)-C(2) single bonds have lengths of 1.380(5) and 1.381(6) Å, respectively. There is a delocalized double bond over the N(1)-C(3)-N(2) part of the ring, with bonds N(1)-C(3) = 1.341(5) Å and N(2)-C(3) = 1.342(6) Å. The bond angle around C(4) of 111.3(3)° is larger than the ideal of 109.5° for a sp^3-hybridised carbon atom, contributing to the larger bite angle of tmi^- [N(1)-Re-S = 81.8(1)°], and the N(1)-C(3)-C(4)-S torsion angle equals 2.3(6)°.

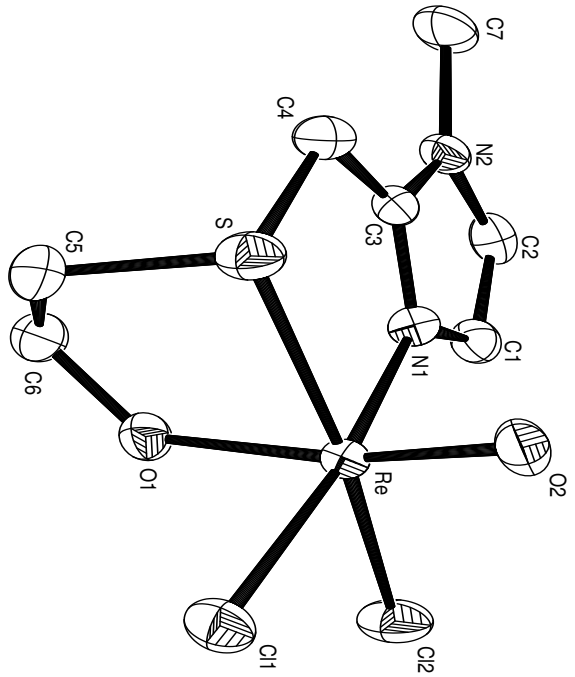


Figure 1. An ORTEP view of $[ReOCl_2(tmi)]$ (**1**), showing the atom labelling scheme and 50% probability ellipsoids.

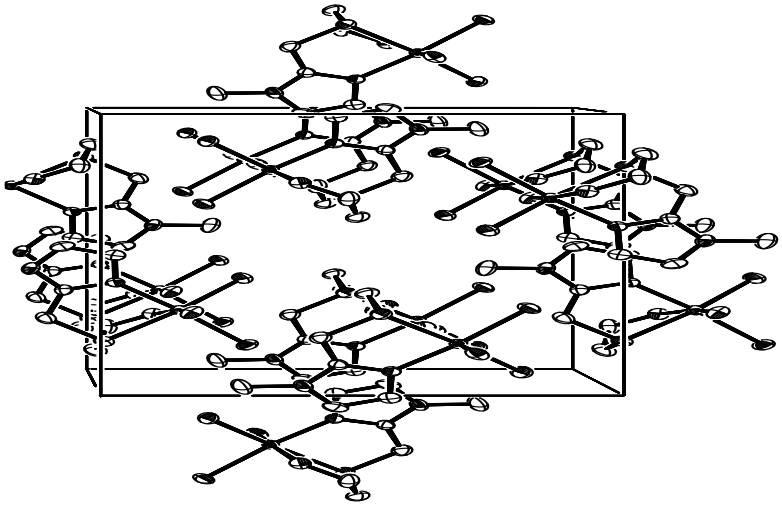


Figure 2. The packing diagram of $[ReOCl_2(tmi)]$ (**1**), shown along the (1,0,0) axis.

Table 2. Selected bond lengths (Å) and bond angles (°) for **1**.

Re-O(2)	1.696(3)	C(6)-O(1)	1.406(6)
Re-O(1)	1.911(3)	C(4)-S	1.825(5)
Re-N(1)	2.082(6)	N(1)-C(3)	1.341(5)
Re-S	2.450(1)	N(2)-C(3)	1.342(6)
Re-Cl(1)	2.41(1)	C(1)-C(2)	1.356(7)
Re-Cl(2)	2.37(1)	C(5)-C(6)	1.515(8)
O(1)-Re-O(2)	165.8(1)	O(2)-Re-N(1)	92.3(2)
Cl(1)-Re-N(1)	173.5(1)	O(1)-C(6)-C(5)	109.3(4)
Cl(2)-Re-S	169.61(4)	C(5)-S-C(4)	103.4(2)
Cl(1)-Re-Cl(2)	89.76(4)	N(1)-C(3)-C(4)	125.0(4)
N(1)-Re-S	81.82(9)	Re-N(1)-C(3)	121.1(3)
S-Re-O(1)	79.28(8)	C(3)-N(2)-C(2)	108.2(4)
O(2)-Re-Cl(1)	92.6(1)	C(1)-C(2)-N(2)	106.7(4)
O(2)-Re-Cl(2)	102.9(1)	O(1)-Re-N(1)	86.5(1)
O(2)-Re-S	86.6(1)	Re-O(1)-C(6)	129.6(3)

The axial Re-O(1) bond [1.911(3) Å] is slightly longer than those found for Re(V)-O (ethoxide) bonds [1.880(6)-1.896(6) Å], where significant multiple bonding has been postulated and is substantially less than the range of 2.00-2.08 Å which is considered to be representative of Re(V)-O single bonds, and it indicates some double-bond character for this bond [9, 17, 18]. Another indication of its double bond character is that the Re-O(1)-C(6) angle is splayed to 129.6(3)° when no apparent intramolecular nonbonding contacts exist, which is close to the expected 120° for Re(V)-O double bonds [9]. The Re = O(2) [1.696(3) Å] shows high double-bond character and is within a range that is expected for mononuclear octahedral oxorhenium(V) complexes (Table 3) with an anionic oxygen donor atom *trans* to the oxo ligand [17-20]. The Re-Cl(1) distance [2.41(1) Å] is markedly longer than the Re-Cl(2) bond [2.37(1) Å], indicating the greater *trans* influence of the imidazole ring compared to the sulfur atom.

Table 3. Comparison of spectral and structural data of oxorhenium(V) complexes containing the tridentate imidazole ligands.

Complex	$[ReOCl_2(ami)]$ [20]	$[ReOCl_2(L\text{-}his)]$[18]	$[ReOCl_2(tmi)]$ (**1**)
ν(Re=O) (cm^{-1})	942	960	945
ν(Re-N) (cm^{-1})	468	not given	470
ν(Re-Cl) (cm^{-1})	338	not given	320, 318
Re=O (Å)	1.691(5)	1.660(6)	1.696(3)
Re-O (Å)	1.901(5)	2.081(6)	1.911(3)
Re-N(im) (Å)	2.062(8)	2.099(8)	2.082(3)
Re-Cl (Å)	2.440(3), 2.363(2)	2.351(3), 2.334(2)	2.41(1), 2.37(1)
O=Re-O (°)	164.8(3)	162.8(3)	165.8(1)°

Gerber and co-workers have previously isolated the complex $[ReOCl_2(L)]$, where L^- is an *NNO*-donor ligand (HL = 2-[[{2-(2-pyridinyl)ethyl}amino]methyl]phenol) containing a phenolate oxygen, secondary amino nitrogen and a pyridyl nitrogen as donor atoms [19]. A similar complex, $[ReOCl_2(ami)]$ [Hami = 2-(1-ethanolaminomethyl)-1-methylimidazole], has also been isolated and fully characterized, where ami^- is a tridentate ligand containing an alcoholate oxygen, secondary amino nitrogen and an imidazolyl nitrogen as donor atoms [20]. In addition to the tridentate imidazole ligands, Beauchamp and co-workers have isolated the neutral mononuclear complexes $[ReOX_2(L\text{-}his)]$ (X = Cl, Br), where L-hisH is the non-sulfur-containing amino acid histidine with a carboxylic oxygen, amino nitrogen and an imidazolyl

nitrogen as donor atoms [18]. X-ray structural studies reveal a *cis* arrangement of the halides and the coordination of the carboxylate oxygen *trans* to the oxo group.

Supplementary data

CCDC-299049 contains the crystallographic data of **1**. These data can be obtained free of charge at www. ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)12234-336033; e-mail: deposit@ccdc.cam.ac.uk].

REFERENCES

1. Dilworth, J.R.; Parrott, S.J. *Chem. Soc. Rev*. **1998**, 27, 43.
2. Blauenstein, P. *New J. Chem.* **1990**, 14, 405.
3. Ohmori, J.; Shimizu-Sasamata, M.; Okade, M.; Sakamoto, S. *J. Med. Chem*. **1996**, 39, 3971.
4. Place, C.; Zimmermann, J.-L.; Mulliez, E.; Guillot, G.; Bois, C.; Chottard, J.-C. *Inorg. Chem*. **1998**, 37, 4030.
5. Várnagy, K.; Sóvágó, I.; Ágoston, K.; Likó, Z.; Süli-Vargha, H.; Sanna, D.; Micera, G. *J. Chem. Soc. Dalton Trans*. **1994**, 2939.
6. Kesicki, E.A.; DeRosch, M.A.; Freeman, L.H.; Walton, C.L.; Harvey, D.F.; Trogler, W.C. *Inorg. Chem*. **1993**, 32, 5881.
7. Dondríguez-Argülles, M.C.; López-Silva, E.C.; Sanmartín, J.; Bacchi, A.; Pelizzi, C.; Zani, F. *Inorg. Chim. Acta* **2004**, 357, 2543, and references therein.
8. Gerber, T.I.A.; Hosten, E.; Tshentu, Z.R.; Mayer, P.; Pérez-Carreño, E.; Garcia-Granda, S.; Du Preez, J.G.H. *J. Coord. Chem.* **2003**, 56, 1063.
9. Gerber, T.I.A.; Tshentu, Z.R.; Mayer, P. *J. Coord. Chem.* **2003**, 56, 1357.
10. Lis, T.; Jezowska-Trzebiatowska, B. *Acta Cryst*. **1977**, B33, 1248**.**
11. Mtotywa, M.M. *Ph.D. Thesis*, University of Port Elizabeth, South Africa; **2002**.
12. Sheldrick, G.M. *SHELXL-97*, Programs for Structure Solution and Refinement; University of Göttingen; Germany, **1997**.
13. Geary, W.J. *Coord. Chem. Rev.* **1971**, 7, 81.
14. Banberry, H.J.; McQuillan, F.; Hamor, T.A.; Jones, C.J.; McCleverty, J.A. *J. Chem. Soc., Dalton Trans.* **1989**, 1405.
15. Lane, T.J.; Nakagawa, I.; Walker, J.L.; Kandathil, A.J. *Inorg. Chem.* **1962**, 1, 267.
16. Reedijk, J. *J. Inorg. Nucl. Chem.* **1971**, 33, 179.
17. Gerber, T.I.A.; Luzipo, D.; Mayer, P. *J. Coord. Chem.* **2003**, 56, 1549.
18. Tessier, C.; Rochon, F.D.; Beauchamp, A.L. *Inorg. Chem.* **2002**, 41, 6527.
19. Abrahams, A.; Bandoli, G.; Gatto, S.; Gerber, T.I.A.; Du Preez, J.G.H. *J. Coord. Chem*. **1997**, 42, 303.
20. Gerber, T.I.A.; Mayer, P.; Tshentu, Z.R. *J. Chem. Cryst.* **2005**, 35, 35.