

Bi- and tetranuclear oxidorhenium(V) complexes with a bipodal pyrrolylthioureato ligand

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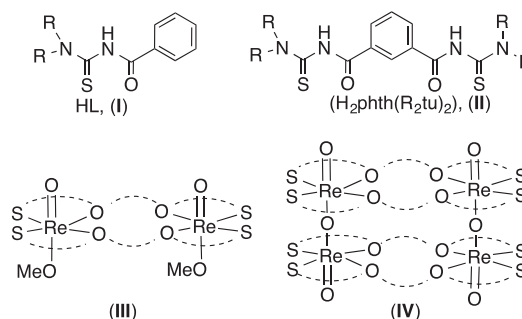
ABSTRACT

A novel aroylbisthiourea, $H_3\text{pyr}(\text{Et}_2\text{tu})_2$ (**V**), has been prepared from 2,5-pyrroledicarboxylic chloride, NH_4SCN and diethylamine. The compound reacts with $(\text{NBu}_4)[\text{ReOCl}_4]$ in MeOH under formation of the dimeric oxidorhenium(V) complex $[\{\text{ReO}(\text{OMe})\}_2\{\text{Hpyr}(\text{Et}_2\text{tu})_2\}_2]$ (**VI**), which undergoes a condensation in wet acetonitrile and forms the μ -oxido-bridged tetramer $[(\text{Re}_2\text{O}_3)_2\{\text{Hpyr}(\text{Et}_2\text{tu})_2\}_4]$ (**VII**). The pyrrole rings remain protonated and do not contribute to the coordination of the transition metal. The tetrameric complex is able to accommodate a molecule of water in its molecular cavity.

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1. Introduction

The coordination chemistry of rhenium and technetium with potentially bidentate 1,1-dialkylbenzoylthioureas (HL, **I**) and related ligands has been described in detail during the recent years. *S,O*-Chelates with singly deprotonated ligands are known for Re(I), Re(III) and Re(V) [1–8]. The corresponding mononuclear oxidorhenium(V) complexes $[\text{ReO}(\text{S,O-L})_2(\text{OMe})]$ undergo a reversible hydrolytic dimerization under formation of $[\{\text{ReO}(\text{S,O-L})_2\}_2\text{O}]$ complexes with linear μ -oxido ligands [3]. A similar behavior is observed for ReO complexes with bipodal 3,3',3'-tetraalkyl-1,1'-isophthaloyl bis(thioureas) ($\text{H}_2\text{phth}(\text{R}_2\text{tu})_2$, **II**), which establish bi- or tetranuclear compounds (**III** and **IV**) [9]. The latter ones possess a cage-like structure. However, the voids between the eight central oxygen donors, which have an approximate diameter of six angstroms, are empty in such compounds [9].



In continuation of this work, we started to modify the ligands **II** in order to extend the coordination abilities of such systems. The addition of a third acylthiourea unit to the central aromatic ring should give access to two-dimensional coordination networks, while the use of a heterocyclic ring system such as pyridine, pyrrole, furan or thiophene might enable the resulting ligand systems to coordinate additional metal ions or to establish hydrogen bonds to appropriate host molecules. To the best of our knowledge, there exists only one published structural report about a metal complex of such a system: a cationic coordination polymer with $\text{Ag}(\text{I})$, in which the metal ions exclusively coordinate to the sulfur donor atoms [10]. Here, we present synthesis and structural

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characterization of the corresponding pyrrole derivative $\text{H}_3\text{pyr}(\text{Et}_2\text{tu})_2$ (**V**) together with its di- and tetranuclear rhenium complexes.

2. Results and discussion

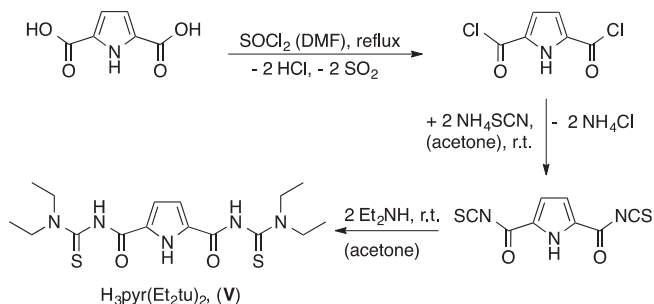
2.1. Synthesis and structure of the proligand

$\text{H}_3\text{pyr}(\text{Et}_2\text{tu})_2$ (**V**) can be prepared from 2,5-pyrroledicarboxylic chloride following the standard route for the synthesis of aroylthioureas [11] by the subsequent addition of NH_4SCN and diethylamine in dry acetone as is shown in Scheme 1. The pale yellow product is readily soluble in acetone, CH_2Cl_2 or CHCl_3 , but only sparingly soluble in alcohols. IR absorptions at 3454 cm^{-1} and 3126 cm^{-1} can be assigned to the NH stretches of the thiourea and the pyrrole moieties. The intense band at 1679 cm^{-1} is due to the stretching vibrations of the $\text{C}=\text{O}$ groups. The ^1H NMR spectrum of **V** in CDCl_3 shows a broad signal at 8.65 ppm (2H) and a sharp singlet at 7.26 ppm (1H), which can be assigned to the NH protons of the thiourea moiety and the pyrrole. A broad signal at 1.32 ppm can be assigned to the methyl protons, and two broad signals at 3.61 and 4.00 ppm to the CH_2 protons. The observed line broadening and splitting of the ethyl signals is due to a hindered rotation around the $\text{C}-\text{NEt}_2$ bonds and has also been reported previously for other *N,N*-dialkyl-*N'*-benzoylthioureas [3].

Single crystals of the compound could be obtained from a CH_2Cl_2 /methanol mixture. Fig. 1 depicts an ellipsoid representation of the molecular structure of **V**. Selected bond lengths and angles are given in Table 1. The $\text{C}-\text{O}$ and $\text{C}-\text{S}$ bond lengths of $1.226(2)/1.228(2)$ and $1.670(2)/1.680(2)\text{ \AA}$, respectively, are in the range of corresponding double bonds. All $\text{C}-\text{N}$ bonds in the backbone of the bipodal aroylthiourea are within the range between 1.35 and 1.42 \AA , which suggests a significant delocalization of π -electron density. The partial double bond character of these bonds is in accordance with the situation in other aroylthioureas [3] and the detection of hindered rotations around the $\text{C}12-\text{N}12$ and $\text{C}22-\text{N}22$ bonds in the NMR spectra of **V**.

2.2. Synthesis and structures of the complexes

Reactions of $\text{H}_3\text{pyr}(\text{Et}_2\text{tu})_2$ with $(\text{NBu}_4)[\text{ReOCl}_4]$ in MeOH and subsequent recrystallization from CH_2Cl_2 /MeOH result in the formation of a red solid (**VI**, Scheme 2). The compound is soluble in dichloromethane, THF and chloroform and almost insoluble in alcohols. The IR spectrum of the complex shows a $\nu_{\text{Re}=\text{O}}$ vibration at 947 cm^{-1} and a bathochromic shift of the $\nu_{\text{C}=\text{O}}$ band with respect to its position in the uncoordinated thiourea derivative **V** (1498 versus 1679 cm^{-1}). The latter fact strongly indicates the formation of *S,O* chelate rings with deprotonated aroylthiourea units as has been observed for other Re(V) and Tc(V) complexes [1,3,9]. A band at 3460 cm^{-1} can be assigned to the NH vibration and indicates that the pyrrole rings remain protonated. This fact is



Scheme 1.

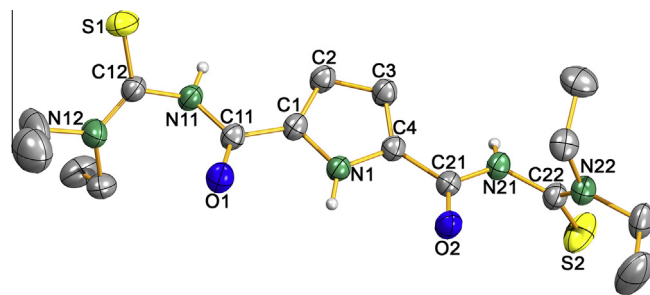


Fig. 1. Ellipsoid representation of the molecular structure of **V** [12]. Thermal ellipsoids represent 50% probability.

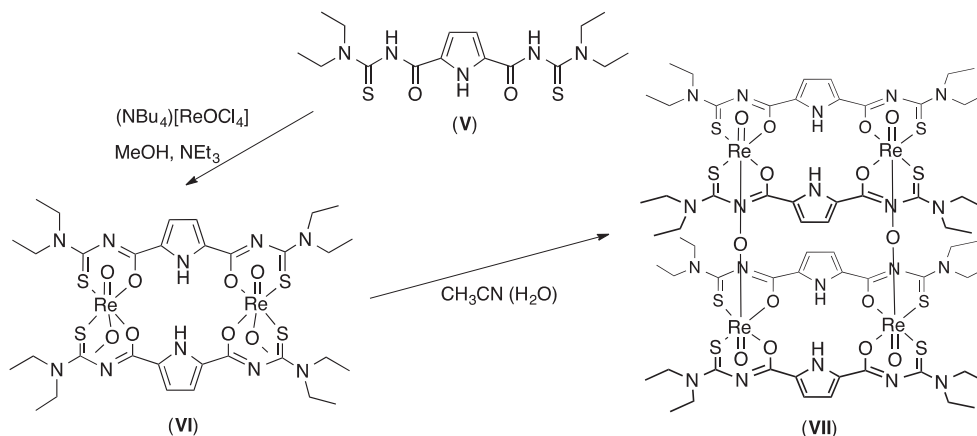
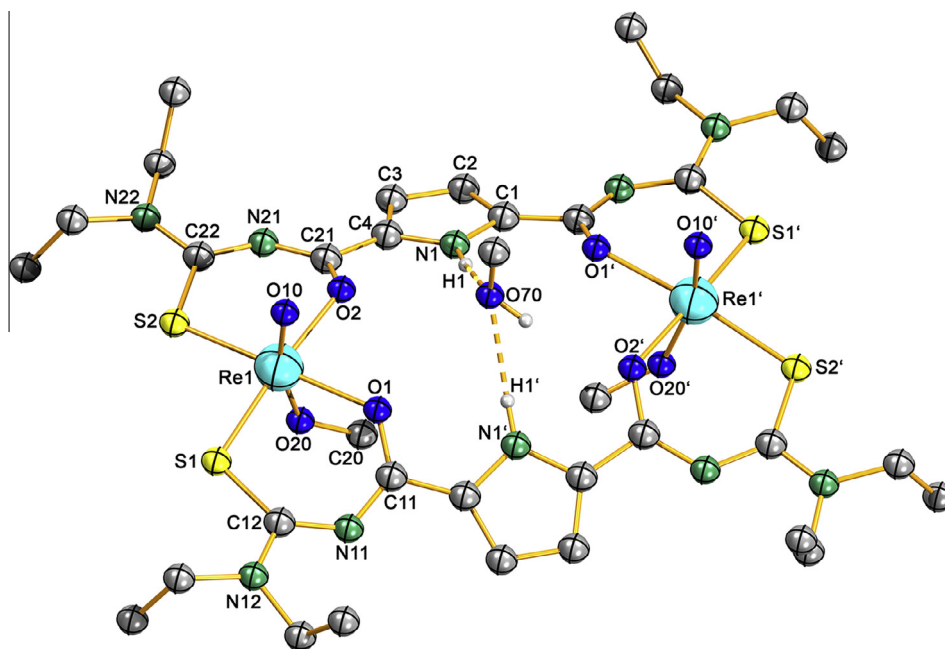
supported by the ^1H NMR spectrum of **V** in CDCl_3 , which shows a NH signal at 7.25 ppm. The compound is stable in this solvent and does not show evidence for hydrolysis. The ethyl signals of the thiourea moieties appear as broad, poorly resolved multiplets, which can be explained by a hindered rotation around the $\text{C}-\text{NEt}_2$ bonds, but might also be due to the appearance of *syn/anti* isomers in solution. Details about the equilibria, which may allow *syn/anti* isomerization between such compounds have been explained and visualized for the corresponding phthaloyl compounds before [9]. Partial multiple-bond character of the $\text{C}-\text{NR}_2$ bonds as source of hindered rotation is frequently found for aroylthioureas and their metal chelates [3]. A rotational barrier of $\Delta G = 15.5\text{ kcal/mol}$ was determined for the uncoordinated *N,N*-diethyl-*N'*-benzoylthiourea, and an increase of this value was detected upon coordination to transition metal ions such as Ni^{2+} , Pd^{2+} or Co^{2+} [13,14].

The spectroscopic data are supported by the results of an X-ray diffraction study. Red single crystals of **VI** could be obtained as CH_2Cl_2 / CH_3OH solvate by recrystallization from a 1/1 mixture (v/v) of these solvents. Expectedly, the product is a dinuclear complex with two $\{\text{ReO}(\text{OMe})\}^{2+}$ units being coordinated by the *S,O* donor atoms of the aroylthiourea units of **V**. The molecular structure of the compound is depicted in Fig. 2 and is similar to that of the corresponding phthaloyl compounds [9]. Bond lengths and angles (Table 2) are unexceptional and correspond to values found earlier for other oxidorhenium(V) complexes with aroylthioureaato ligands [3–9]. This means that the chelate rings show a high degree of delocalized π -electron density and that the $\text{C}-\text{N}$ bonds of the backbone of the ligands are almost equal in lengths. The two pyrrole rings are not coplanar and the hydrogen atoms bonded to the nitrogen atoms establish hydrogen bonds to the solvent methanol, which is arranged above the center of the complex molecule. The $\{\text{ReO}(\text{OMe})\}^{2+}$ units show a relatively long $\text{Re}-\text{O}10$ bond of $1.694(5)\text{ \AA}$ and a short $\text{Re}-\text{O}20$ bond of $1.880(5)\text{ \AA}$. This is characteristic of alcoholato ligands in *trans* position to oxido ligands and can be understood by the transfer of some π -electron density into the $\text{Re}-\text{O}20$ bond, which is supported by the relatively large $\text{Re}-\text{O}20-\text{C}21$ angle of 161.9° . The methoxido ligands are in *syn* arrangement, which allows the formation of oxido bridges between each two rhenium atoms by a controlled hydrolysis and subsequent condensation of the resulting hydroxido ligands.

Such a hydrolysis/condensation is achieved by recrystallization from acetonitrile/ H_2O . The resulting green crystals of **VII**· H_2O are only sparingly soluble in common organic solvents, which prevents the measurement of NMR spectra of reasonable quality. But the shift of the IR $\nu_{\text{Re}=\text{O}}$ frequency from 947 to 904 cm^{-1} and the appearance of an additional band at 660 cm^{-1} are characteristic of the $\{\text{O}=\text{Re}-\text{O}-\text{Re}=\text{O}\}^{4+}$ core. The formation of this core is not unusual in the coordination chemistry of oxidorhenium(V) compounds when charge compensation is one of the driving forces [15], and has also been observed for complexes with aroylthiourea ligands [3,9].

Table 1Selected bond lengths (Å) and angles (°) in **V**.

C11–O1	1.228(1)	C12–S1	1.680(2)	C11–N11	1.359(2)
C21–O2	1.226(2)	C22–S2	1.669(2)	C21–N21	1.357(2)
N11–C12	1.422(3)	C22–N22	1.328(2)		
C1–C11–O1	121.5(2)	N11–C11–O1	122.3(2)	C1–C11–N11	116.2(2)
C4–C21–O2	121.2(2)	N21–C21–O2	123.6(2)	C4–C21–N21	115.1(2)
N11–C12–S1	117.8(1)	N12–C12–S1	125.9(2)	N11–C12–N12	116.3(2)
N21–C22–S2	118.1(1)	N22–C22–S2	127.0(1)	N21–C22–N22	114.9(2)
C11–N11–C12	122.2(2)	C21–N21–C22	123.3(2)		

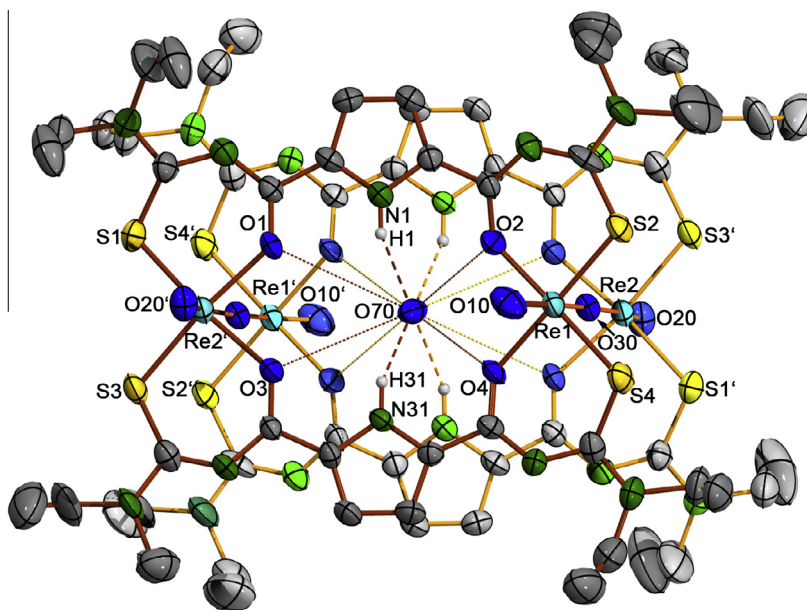
**Scheme 2.****Fig. 2.** Ellipsoid representation of the **VI**-MeOH unit [12]. Thermal ellipsoids represent 50% probability.

A structural study on **VII** confirms the formation of a tetrameric compound with two oxido bridges. Fig. 3 shows the molecular structure of the complex. Bond lengths and angles are similar to

those in the precursor molecule **VI**, and also the pyrrole nitrogen atoms remain protonated in the tetramer. Selected bonding parameters of **VII** are contained in Table 3. The oxido bridges are

Table 2Selected bond lengths (Å) and angles (°) in **VI**.

Re1–O10	1.694(5)	Re1–O20	1.880(5)	C11–N11	1.322(8)
Re1–O1	2.123(4)	O1–C11	1.293(7)	C12–N11	1.338(9)
Re1–O2	2.122(4)	O2–C21	1.286(7)	C21–N21	1.325(8)
Re1–S1	2.328(2)	S1–C12	1.751(6)	C22–N21	1.334(8)
Re1–S2	2.331(2)	S2–C22	1.759(6)		
O10–Re1–O1	85.2(2)	Re1–O1–C11	126.0(4)	Re1–O2–C21	126.3(4)
O10–Re1–O2	85.3(2)	O1–C11–N11	129.3(6)	O2–C21–N21	129.8(6)
O10–Re1–S1	99.0(2)	C11–N11–C12	126.5(6)	C21–N21–C22	127.2(5)
O10–Re1–S2	99.4(2)	N11–C12–S1	129.3(5)	N21–C22–S2	128.7(5)
O10–Re1–O20	163.1(3)	C12–S1–Re1	107.2(2)	C22–S2–Re1	107.7(2)
<i>Hydrogen bonds</i>					
N1–H1	0.860	H1...O70	2.011	N1...O70	2.862(8)
				N1–H1...O70	170.4

**Fig. 3.** Ellipsoid representation of the structure of **VII**·H₂O [12]. Thermal ellipsoids represent 50% probability.**Table 3**Selected bond lengths (Å) in **VII**. The values are given for two symmetry-independent species.

Re1–O10	1.693(6)/1.702(5)	Re2–O20	1.686(6)/1.693(5)
Re1–O30	1.890(5)/1.884(5)	Re2–O30	1.928(5)/1.929(5)
Re1–O2	2.124(5)/2.135(5)	Re2–O1	2.096(4)/2.090(4)
Re1–O3	2.134(4)/2.145(5)	Re2–O4	2.088(5)/2.088(5)
Re1–S2	2.328(2)/2.319(2)	Re2–S1	2.354(2)/2.342(2)
Re1–S3	2.331(2)/2.322(2)	Re2–S4	2.348(2)/2.354(2)
<i>Hydrogen bonds</i>			
N1–H1	0.860	H1...O70	2.313
N31–H31	0.860	H31...O70	2.862(8)
		N1...O70	3.041
		N1...O70	3.052
		N1–H1...O70	145.2
		N1–H1...O70	144.4

almost linear with Re–O–Re angles of 178.2(3) and 179.0(4)°. This is in agreement with other compounds of this type and allows the transfer of electron density into the oxido bridges [15].

An apparent difference between the structures of the complexes of the present study is the orientation of the central pyrrole rings of the opposite ligands. The planes defined by the two pyrrole ring systems form an angle of 129.7(3)° in compound **VI**, which allows their NH hydrogen atoms to establish efficient hydrogen bonds to the exocyclic methanol. In compound **VII**, they are slightly tilted toward each other with the NH hydrogen atoms pointing to the

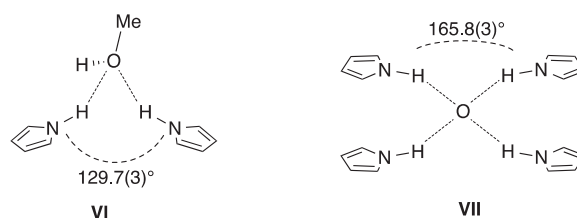
**Scheme 3.**

Table 4

X-ray structure data collection and refinement parameter.

	V	VI ·2CH ₂ Cl ₂ ·MeOH	VII ·H ₂ O
Formula	C ₁₆ H ₂₅ N ₅ O ₂ S	C ₃₇ H ₆₀ N ₁₀ Cl ₄ O ₉ S ₄ Re ₂	C ₆₂ H ₈₄ N ₂₀ O ₁₄ S ₈ Re ₄
<i>M_w</i>	383.53	1431.39	2374.79
Crystal system	monoclinic	monoclinic	triclinic
<i>a</i> (Å)	25.341(2)	18.788(1)	15.517(5)
<i>b</i> (Å)	12.821(2)	7.754(1)	16.385(5)
<i>c</i> (Å)	13.190(1)	20.767(2)	18.881(5)
α (°)	90	90	86.11(1)
β (°)	109.43(1)	98.68(1)	86.68(1)
γ (°)	90	90	61.89(1)
<i>V</i> (Å ³)	4041.3(4)	2990.6(3)	4223(2)
Space group	C2/c	<i>P</i> 2/ <i>n</i>	<i>P</i> $\bar{1}$
<i>Z</i>	8	2	2
<i>D</i> _{calc} . (g cm ^{−3})	1.260	1.590	1.868
μ (mm ^{−1})	0.282	4.413	5.983
No. of reflections	5410	12 611	48 337
No. of independent	3724	6395	12 391
No. parameters	246	328	997
<i>R</i> ₁ / <i>wR</i> ₂	0.0549/0.1625	0.0415/0.0916	0.0437/0.0800
Goodness-of-fit (GOF)	1.011	0.942	0.796

center of the void between the four rhenium atoms (Scheme 3). The void is occupied by a molecule of water, which is fixed by hydrogen bonds to the oxygen and nitrogen atoms of the ligands (Fig. 3).

3. Conclusions

Ligands of the type **V** are well suited for the coordination of oxidorhenium(V) cores. The NH hydrogen atoms of the pyrrole rings are not deprotonated in the products and form hydrogen bonds to solvent molecules. Deprotonation of the pyrrole rings or replacement of the aromatic rings by pyridine, furan or thiophene may form cage-like structures such as **VII**, which are able to host 'hard' metal ions in the central void. Corresponding studies are currently undertaken in our laboratories.

4. Experimental

4.1. Materials

All reagents used in this study were reagent grade and used without further purification.

4.2. Physical measurements

Infrared spectra were measured from KBr pellets on a Shimadzu FTIR-spectrometer or a Nicolet FTIR 670 instrument between 400 and 4000 cm^{−1}. ESI mass spectra were measured with an Agilent 6210 ESI-TOF (Agilent Technologies). All MS results are given in the form: *m/z*, assignment. Elemental analysis of carbon, hydrogen, nitrogen, and sulfur were determined using a Heraeus Vario EL elemental analyzer. NMR-spectra were taken with a JEOL 400 MHz multinuclear spectrometer.

4.3. Syntheses

4.3.1. Synthesis of H₃pyr(Et₂tu)₂ (**V**)

2,5-Pyrroledicarboxylic acid (5 g, 13.1 mmol) was mixed with 20 ml SOCl₂ and 4 drops DMF and heated on reflux for 4 h. After complete removal of the solvent, the remaining solid was dissolved in 15 ml dry acetone and added dropwise to a solution of NH₄SCN (1.98 g, 26 mmol) in 20 ml dry acetone. The mixture was stirred at room temperature for 2 h and added to a solution of diethylamine (1.9 g, 26 mmol) in 10 ml acetone. The mixture was stirred for

another hour and the product was precipitated as a pale yellow solid by the addition of 150 ml water. A crystalline product was obtained by recrystallization from CH₂Cl₂/MeOH. Yield: 52%. Melting point: 164–166 °C. Elemental analysis: *Anal.* Calc. for C₁₆H₂₅N₅O₂S₂: C, 50.1; H, 6.6; N, 18.2. Found: C, 49.4; H, 6.4; N, 17.7%. IR (cm^{−1}): 3454 (w), 3254 (m), 3126 (m), 2975 (w), 2934 (w), 1679 (s), 1654 (m), 1550 (s), 1475 (s), 1265 (s), 1218 (vs), 843 (w), 813 (w), 763 (w). ¹H NMR (CDCl₃; δ , ppm): 1.32 (m, 12H, CH₃); 3.61 (broad, 4H, CH₂); 4.00 (m, 4H, CH₂); 6.79 (s, 2H, CH_{arom}); 7.26 (s, 1H, NH_{arom}); 8.65 (s, 2H, NH_{thiourea}). ESI⁺ MS (*m/z*): 384 [M+H]⁺, 406 [M+Na]⁺, 422 [M+K]⁺.

4.3.2. Synthesis of **VI**

(NBu₄)[ReOCl₄] (0.2 mmol, 116 mg) in 3 ml MeOH was added to a solution of H₃pyr(Et₂tu)₂ (0.2 mmol, 76.6 mg) in 3 ml MeOH. Three drops of NEt₃ were added and the mixture was stirred for 30 min at 40 °C. After cooling to room temperature, the formed solid was filtered off and washed with MeOH. Recrystallization from CH₂Cl₂/MeOH gave orange-red crystals. Yield: 80%. Elemental analysis for the microcrystalline, solvent-less, carefully dried compound: *Anal.* Calc. for C₃₄H₅₂N₁₀O₈S₄Re₂: C, 33.2; H, 4.3; N, 11.4; S, 10.4. Found: C, 33.6; H, 4.3; N, 11.6; S, 10.7%. IR (cm^{−1}): 3460 (w), 2977 (w), 2932 (w), 2361 (w), 1498 (s), 1449 (m), 1390 (s), 1351 (s), 1264 (m), 1200 (m), 1090 (m), 947 (m), 872 (w), 806 (w), 676 (w), 759 (w). ¹H NMR (CDCl₃; δ , ppm): 1.22 (m, 24H, CH₃); 3.11 (m, 6H, CH₃ methoxide), 3.67–3.89 (m, 8H, CH₂); 6.85 (s, 1H, CH_{arom}); 6.88 (s, 1H, CH_{arom}); 7.26 (s, 1H, NH_{arom}). ESI⁺ MS: *m/z* = 1167 [M–2OMe+H]⁺, 1189 [M–2OMe+Na]⁺, 1250 [M–2OMe+K]⁺.

4.3.3. Synthesis of **VII**

A solution of **VI** (0.02 mmol, 34 mg) in 5 ml CHCl₃ was treated with 1 ml of CH₃CN and 3 drops of water and stirred for 1 h at room temperature. During this time, its color changed to green and green crystals of **VII**·H₂O deposited after slow evaporation of the solvents. Yield: 36 mg, 0.015 mmol. Elemental analysis: *Anal.* Calc. for C₆₄H₈₄N₂₀O₁₄S₈Re₄: C, 32.6; H, 3.6; N, 11.9; S, 10.9. Found: C, 33.0; H, 3.4; N, 11.8; S, 10.7%. IR (cm^{−1}): 2976 (w), 2933 (w), 2865 (w), 1496 (s), 1389 (s), 1346 (m), 1259 (m), 1196 (w), 1142 (w), 1068 (m), 1006 (w), 938 (w), 904 (w), 873 (w), 807 (m), 756 (m), 713 (m), 660 (m), 564 (w), 533 (m). ESI⁺ MS (*m/z*): 2367 [M+H]⁺, 1189 [M/2]⁺, 1167 [M/2–O]⁺.

4.4. X-ray crystallography

The intensities for the X-ray determinations were collected on a Bruker CCD X8 Kappa APEX II (**V**) or a STOE IPDS 2T instrument (**VI** and **VII**) with Mo K α radiation ($\lambda = 0.71073$ Å). Standard procedures were applied for data reduction and absorption correction. Structure solution and refinement were performed with SHELXS and SHELXL [16]. Hydrogen atom positions were calculated for idealized positions and treated with the 'riding model' option of SHELXL.

More details on data collections and structure calculations are contained in Table 4.

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Appendix A. Supplementary data

CCDC 1016090, 1016091 and 1016092 contain the supplementary crystallographic data for **V**, **VI**·2 CH₂Cl₂·MeOH and **VII**·H₂O respectively. 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.

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