Inorganica Chimica Acta, 204 (1993) 195–198

The reaction of $CpRu(PPh_3)_2^+$ with organic thiols. Synthesis and characterization of $[CpRu(PPh_3)_2(RSH)]BF_4$ (R = benzyl, phenethyl) and the molecular and crystal structure of $[CpRu(PPh_3)_2(C_6H_5CH_2CH_2SH)]BF_4 \cdot CH_2Cl_2$

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(Received September 1, 1992)

Abstract

The isolation and characterization of two mercaptan complexes of the general formula $[CpRu(PPh_3)_2(RSH)]BF_4$, where R = benzyl and phenethyl, were undertaken to model the substrate/catalyst interaction of the hydrodesulfurization (HDS) process. The IR data show a shift in the S–H stretching frequency upon coordination. The structure of the $[CpRu(PPh_3)_2(C_6H_5CH_2CH_2SH)]BF_4$ complex was determined by X-ray diffraction techniques: monoclinic space group $P2_1/n$, $a = 15.317(4)$, $b = 13.924(9)$, $c = 21.815(7)$ Å, $\beta = 95.20(2)°$, $Z = 4$, $R = 0.057$, $R_w = 0.073$. The Ru is attached to two triphenylphosphine ligands, a cyclopentadienyl and the phenethylmercaptan. The Ru–S distance is 2.369(2) Å and the S–H distance is 1.18 Å.

Introduction

The treatment of fossil fuels prior to the refining process is necessary to remove heteroatom impurities such as S to prevent poisoning of reformation catalysts [1, 2]. Sulfur impurities include organic thiols, sulfides, disulfides and thiophene derivatives [3]. The removal of sulfur or hydrodesulfurization (HDS) is achieved by employing a sulfided metal catalyst at elevated temperatures in the presence of H_2 at high pressures [4]. The exact mechanism for this process is currently unknown [5, 6]. Model studies for the substrate–catalyst interactions have focussed mainly on the complexation of the thiophenic moiety to a metal center [7–9].

The affinity of Ru^{2+} for sulfur [10] plus the finding that RuS_2 is one of the best catalysts for desulfurization of dibenzothiophene [11–13] lead us to the investigation of the coordination of organic thiols to a $CpRu(PPh_3)_2^+$ fragment. Rauchfuss and co-workers have demonstrated the ability to attach weak S-donor ligands to $CpRu(PPh_3)_2^+$ [14–17]. Herein the synthesis of two ruthenium mercaptan complexes, $[CpRu(PPh_3)_2(RSH)]BF_4$, where R = benzyl and phenethyl, is reported. The crystal and molecular structure of the phenethyl complex will be discussed.

Experimental

Materials and methods

Reactions were carried out under a dry nitrogen atmosphere using Schlenk techniques. $CpRu(PPh_3)_2Cl$ was prepared as described in the literature [18]. All other reagents were used as purchased without further purification. ^1H NMR spectra were obtained on a Chemagnetics A200 spectrometer using tetramethyl silane (TMS) as the reference. IR spectra were obtained on a Nicolet 5PC FT-IR spectrophotometer using KBr or Nujol mulls on NaCl plates. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, USA.

Synthesis of $[CpRu(PPh_3)_2(C_6H_5CH_2SH)]BF_4$ (I)

A 0.2240 g (0.31 mmol) sample of $CpRu(PPh_3)_2Cl$ was dissolved in 10 ml of CH_2Cl_2 and 10 ml of benzylthiol

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0020-1693/93/$6.00

was added. In a darkened room, excess (0.0751 g, 0.39 mmol) $AgBF_4$ was added to the solution while stirring. After 15 min, the solution was concentrated to half volume under vacuum and filtered through Celite. Further concentration of the filtrate gave yellow crystals which were isolated by filtration. The product was washed with diethyl ether and dried. Yield 0.1793 g, 64%. *Anal.* Calc. for $C_{48}H_{43}RuP_2SBF_4$: C, 63.93; H, 4.82; S, 3.56. Found: C, 63.68; H, 4.95; S, 3.76%. ^1H NMR (ppm, in $CDCl_3$): 7.28 (m, 21H), 6.98 (m, 14H), 4.79 (s, 5H), 4.17 (quintet, 1H), 3.81 (d, 2H). IR: ν (SH) = 2525 cm^{-1}.

Synthesis of [CpRu(PPh$_3$)$_2$(C$_6$H$_5$CH$_2$CH$_2$SH)]BF$_4$·CH$_2$Cl$_2$ (II)

A 0.1981 g (0.27 mmol) sample of $CpRu(PPh_3)_2Cl$ was dissolved in 15 ml of CH_2Cl_2 and 0.5 ml of phenethyl mercaptan was added. In a darkened room, excess (0.0645 g, 0.33 mmol) $AgBF_4$ was added to the solution while stirring. After 15 min, the solution was filtered through Celite and the filtrate was concentrated to dryness. Recrystallization from CH_2Cl_2/pentane gave a yellow microcrystalline product. Yield 0.1498 g, 55%. *Anal.* Calc. for $C_{50}H_{47}RuP_2SBF_4Cl_2$: C, 60.00; H, 4.70; S, 3.20. Found: C, 60.00; H, 4.80; S, 3.02%. ^1H NMR (ppm, in $CDCl_3$): 7.69 (m, 3H), 7.49 (m, 2H), 7.21 (m,

TABLE 1. Crystallographic data for $[CpRu(PPh_3)_2(C_6H_5CH_2CH_2SH)]BF_4 \cdot CH_2Cl_2$ (**II**)

Formula	$C_{50}H_{47}RuP_2SBF_4Cl_2$
Formula weight	1000.70
Space group	$P2_1/n$
a (Å)	15.317(4)
b (Å)	13.924(9)
c (Å)	21.815(7)
α (°)	90.00
β (°)	95.20(2)
γ (°)	90.00
V (Å^3)	4633(4)
Z	4
D_{calc} (g/cm^3)	1.44
$F(000)$	2045
μ(mm^{-1})	0.61
Scan type	θ–2θ
Scan range	$1.00 + 0.35 \tan\theta$
Scan speed (°/min)	4.0–16.0
Max. 2θ (°)	25.0
Total reflections	8457
Unique reflections	8133
R_{int}	0.059
Reflections with $I > 4\sigma I$	4529
Parameters	549
R	0.057
R_w	0.073
GOF	1.06
Max. Δ/σ final	0.02
Residual density	−1.24(12), 1.64(12)

TABLE 2. Final positional coordinates and thermal parameters for the non-hydrogen atoms and the thiol hydrogen of $[CpRu(PPh_3)_2(C_6H_5CH_2CH_2SH)]BF_4 \cdot CH_2Cl_2$

Atom	x	y	z	B_{iso}[a]
Ru	0.95132(3)	0.14952(4)	0.780496(24)	2.534(19)
Cl(1)	0.21611(12)	0.66782(21)	0.03265(14)	7.95(15)
Cl(2)	0.3256(3)	0.8261(3)	0.00372(21)	11.40(25)
S	1.08416(12)	0.06942(14)	0.81252(9)	3.60(8)
P(1)	0.93147(12)	0.04965(13)	0.69353(8)	2.83(7)
P(2)	1.02850(12)	0.28113(13)	0.74568(8)	2.95(7)
F(1)	−0.0302(4)	0.2292(6)	1.0799(3)	8.8(4)
F(2)	0.0773(4)	0.1237(4)	1.0726(3)	7.3(3)
F(3)	0.0497(4)	0.2339(4)	0.99901(25)	7.5(3)
F(4)	−0.0455(4)	0.1143(4)	1.00721(24)	6.3(3)
C(1)	0.8250(5)	0.0718(5)	0.6508(3)	3.2(3)
C(2)	0.7569(5)	0.0061(6)	0.6486(4)	4.1(3)
C(3)	0.6757(5)	0.0290(6)	0.6195(4)	4.7(4)
C(4)	0.6607(6)	0.1172(7)	0.5932(4)	4.9(4)
C(5)	0.7258(6)	0.1824(6)	0.5955(4)	4.6(4)
C(6)	0.8069(5)	0.1620(5)	0.6245(4)	4.1(3)
C(7)	0.9247(4)	−0.0451(6)	0.7100(3)	3.0(3)
C(8)	0.9135(5)	−0.1455(6)	0.6614(3)	3.6(3)
C(9)	0.9062(5)	−0.2435(6)	0.6738(4)	4.3(4)
C(10)	0.9108(5)	−0.2756(6)	0.7329(4)	4.2(4)
C(11)	0.9224(5)	−0.2126(6)	0.7810(3)	4.1(3)
C(12)	0.9297(5)	−01156(5)	0.7697(3)	3.3(3)
C(13)	1.0085(5)	0.0433(5)	0.6343(3)	3.7(3)
C(14)	1.0000(6)	0.0950(7)	0.5802(4)	5.7(5)
C(15)	1.0641(10)	0.0885(11)	0.5383(5)	8.7(8)
C(16)	1.1363(10)	0.0317(10)	0.5509(7)	8.5(8)
C(17)	1.1458(7)	−0.0197(8)	0.6027(6)	7.1(6)
C(18)	1.0819(6)	−0.0153(7)	0.6450(4)	5.5(5)
C(19)	1.0414(5)	0.3759(5)	0.8044(3)	3.5(3)
C(20)	1.0717(6)	0.3502(6)	0.8643(4)	4.8(4)
C(21)	1.0879(6)	0.4187(7)	0.9100(4)	5.2(4)
C(22)	1.0751(6)	0.5130(7)	0.8963(5)	5.3(4)
C(23)	1.0452(6)	0.5402(6)	0.8377(5)	5.2(5)
C(24)	1.0295(5)	0.4724(5)	0.7921(4)	4.1(4)
C(25)	0.9773(5)	0.3452(5)	0.6787(3)	3.8(3)
C(26)	0.8925(7)	0.3811(8)	0.6803(4)	6.1(5)
C(27)	0.8500(7)	0.4262(7)	0.6287(5)	6.4(5)
C(28)	0.8919(10)	0.4354(8)	0.5770(5)	7.9(7)
C(29)	0.9741(9)	0.3974(11)	0.5737(5)	8.3(7)
C(30)	1.0164(6)	0.3547(8)	0.6249(4)	5.7(5)
C(31)	1.1437(5)	0.2708(5)	0.7273(3)	3.3(3)
C(32)	1.2037(7)	0.3430(8)	0.7404(6)	7.0(6)
C(33)	1.2886(7)	0.3324(9)	0.7235(6)	7.8(6)
C(34)	1.3135(6)	0.2557(8)	0.6936(5)	6.4(6)
C(35)	1.2550(7)	0.1860(9)	0.6800(6)	7.8(6)
C(36)	1.1705(6)	0.1947(7)	0.6969(5)	6.2(5)
C(37)	1.2538(5)	0.0842(6)	0.9148(4)	4.6(4)
C(38)	1.2553(7)	0.1677(7)	0.9462(4)	5.8(5)
C(39)	1.3200(8)	0.2344(8)	0.9420(6)	7.1(6)
C(40)	1.3853(8)	0.2166(9)	0.9066(7)	8.1(7)
C(41)	1.3849(8)	0.1348(11)	0.8739(8)	10.4(9)
C(42)	1.3196(7)	0.0661(8)	0.8769(7)	7.9(7)
C(43)	1.0913(5)	0.0476(6)	0.8950(4)	4.7(4)
C(44)	1.1807(6)	0.0115(7)	0.9198(5)	5.9(4)
C(45)	0.8778(5)	0.0986(6)	0.8578(4)	4.3(4)
C(46)	0.9056(5)	0.1944(7)	0.8701(3)	4.0(4)
C(47)	0.8654(5)	0.2530(6)	0.8231(4)	4.0(4)
C(48)	0.8145(5)	0.1966(7)	0.7814(4)	4.2(4)
C(49)	0.8213(5)	0.1003(7)	0.8032(4)	4.4(4)
C(50)	0.2295(9)	0.7717(12)	−0.0076(8)	11.6(10)
B	0.0114(7)	0.1762(8)	1.0407(4)	4.9(5)
H(S)	1.148	0.118	0.814	3.2

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoids.

TABLE 3. Selected bond distances (Å) and angles (°) for compound **II**

Bond distances		Bond angles	
Ru–S	2.369(2)	S–Ru–P(1)	90.25(7)
Ru–P(1)	2.349(2)	S–Ru–P(2)	91.07(7)
Ru–P(2)	2.344(2)	P(1)–Ru–P(2)	103.48(7)
Ru–C(45)	2.227(8)	Ru–S–C(43)	110.1(3)
Ru–C(46)	2.224(7)	Ru–S–H(S)	114.9
Ru–C(47)	2.212(7)	C(43)–S–H(S)	95.7
Ru–C(48)	2.198(7)		
Ru–C(49)	2.204(8)		
S–C(43)	1.818(9)		
C(43)–C(44)	1.512(12)		
C(44)–C(37)	1.520(12)		
S–H(S)	1.18		

18H), 6.93 (m, 12H), 4.68 (s, 5H), 3.99 (t, 1H), 2.90 (m, 2H), 2.80 (m, 2H). IR: ν(SH) = 2515 cm^{-1}.

X-ray structure analysis of [CpRu(PPh$_3$)$_2$(C$_6$H$_5$CH$_2$CH$_2$SH)]BF$_4$·CH$_2$Cl$_2$ (II)

Crystals were grown by the slow diffusion of pentane into a CH_2Cl_2 solution of **II**. The crystallographic data are given in Table 1. An amber crystal (0.21 × 0.08 × 0.28 mm) was mounted on a glass fiber with epoxy. All measurements were made on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo K (α) radiation. Cell constants were obtained from a least-squares refinement using the setting angles of 25 reflections in the range $18.0 < 2\theta < 20.0°$. The intensities of three standard reflections which were measured after every 60 min of X-ray exposure time drifted by 1.1%. A total of 8457 reflections (8133 unique reflections, $R_{int} = 0.059$) was collected using the θ–2θ scan technique to a maximum 2θ value of 25°. The data were corrected for Lorentz and polarization effects and an analytical absorption correction was applied. Neutral atom scattering factors were taken from Cromer and Waber [19]. Anomalous dispersion effects were included in F_{calc} [20]; the values of (delta)f' and (delta)f'' were those of Cromer [21].

The structure was solved by direct methods and refined by full matrix least-squares. The final cycle of the full matrix least-squares refinement was based on 4529 observed reflections ($I > 4.00\sigma(I)$) and 549 parameters and converged with $R = 0.057$, $R_w = 0.073$. The hydrogen atoms were constrained to idealized positions (C–H = 0.95 Å) except for the H atom attached to the S, which is reported at a position indicated on a difference map. Final atomic coordinates and equivalent thermal parameters for the non-hydrogen atoms and the thiol hydrogen are given in Table 2. Selected bond distances and angles are given in Table 3.

Results and discussion

The dechlorination of CpRu(PPh$_3$)$_2$Cl with AgBF$_4$ in the presence of the organic thiol leads to the formation of moisture sensitive, yellow products in moderate to good yields. In both cases, the IR spectrum shows a change in the S–H stretch from the free (unbound) mercaptan as compared to the coordinated mercaptan (Table 4). The ν(SH) stretch for the Cr(CO)$_5$(t-butylSH) compound has been assigned to a peak at 2555 cm^{-1} [22]. This is very similar to the value for the S–H stretch observed for the neat t-butyl thiol (Table 4). The S–H stretch was too weak to be observed in the IR spectrum of [CpRu(dppm)(t-C$_4$H$_9$SH)]PF$_6$, however the [CpRu(PPh$_3$)(t-C$_4$H$_9$NC)(t-C$_4$H$_9$SH)]PF$_6$ complex shows a ν(SH) at 2544 cm^{-1} [23].

The proton NMR spectra show resonances as multiplets for the phenyl protons between 6.9 and 7.5 ppm. In compounds **I** and **II**, the *-SH* proton is shifted downfield relative to the free mercaptan resonance. This downfield shift is similar to, though not as large as, the *–SH* chemical shift observed in [CpFe(CO)$_2$(PhSH)]BF$_4$ [24]. Darensbourg *et al.* have noticed slight upfield shifts for the *–SH* resonances in the Cr(CO)$_5$(RSH) compounds, where R = t-butyl, i-propyl and ethyl [22]. For the Ru compounds [CpRu(dppm)(t-C$_4$H$_9$SH)]PF$_6$ and [CpRu(PPh$_3$)(t-C$_4$H$_9$NC)(t-C$_4$H$_9$SH)]PF$_6$, the NMR resonances for the thiol protons are shifted slightly when compared to the free thiols [23].

The structure of **II** shows the Ru atom bound to the Cp, two P atoms of the PPh$_3$ ligands and the S of the phenethyl mercaptan (Fig. 1). The Ru–S distance of 2.369(2) Å in **II** is similar to the Ru–S distance of

TABLE 4. S–H stretching frequencies (cm^{-1}) showing change in frequency upon coordination

Compound	R	Free[a]	Bound	Change
[CpRu(PPh$_3$)$_2$(RSH)]BF$_4$	benzyl	2566	2512	54
[CpRu(PPh$_3$)$_2$(RSH)]BF$_4$	phenethyl	2568	2515	53
Cr(CO)$_5$(RSH)	t-butyl	2558	2555[b]	3
[CpRu(PPh$_3$)(t-C$_4$H$_9$NC)(RSH)]PF$_6$	t-butyl	2558	2544[c]	14

[a] Neat thiol was placed directly on NaCl plates and the spectrum was run. [b] Ref. 22. [c] Ref. 23.

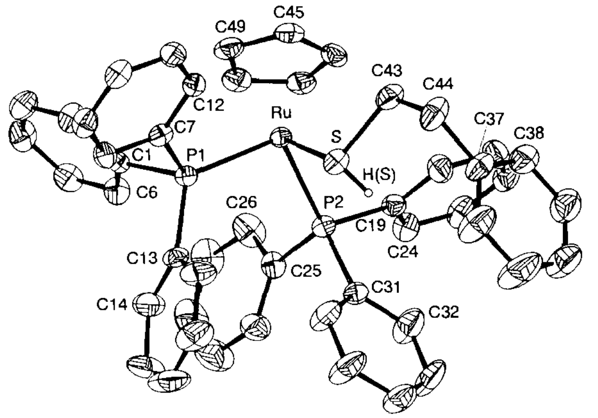

Fig. 1. ORTEP plot (30% probability ellipsoids) of $[CpRu(PPh_3)_2(C_6H_5CH_2CH_2SH)]BF_4 \cdot CH_2Cl_2$ showing cation atom labeling scheme. The hydrogen atoms (except the thiol H) are omitted for clarity. Carbon atoms are numbered sequentially around the phenyl rings in the direction shown.

2.377(2) Å in $[CpRu(PPh_3)_2(n\text{-}C_3H_7SH)]BF_4$ [17] and 2.375(2) Å in $[CpRu(PPh_3)_2(i\text{-}C_4H_9SH)]BF_4$ but is considerably shorter than the Ru–S distance of 2.396(2) Å in $[CpRu(PPh_3)_2(t\text{-}C_4H_9SH)]BF_4$. The longer Ru–S distance in the t-butyl complex may be due to steric effects. The S–H distance in **II** is 1.18 Å. This is shorter than the same distance in $[CpRu(PPh_3)_2(n\text{-}C_3H_7SH)]BF_4$ [17] and in $[CpRu(PPh_3)_2(t\text{-}C_4H_9SH)]BF_4$ (1.25 and 1.289(2) Å, respectively). The S–H distance in $Cr(CO)_5$(t-butylSH) is 1.2(1) Å [22]. The Ru–S distance and S–H distances in $[CpRu(dppm)(t\text{-}C_4H_9SH)]PF_6$ are 2.371(2) and 1.349(77) Å, respectively [23]. In the $[CpRu(dppe)(thiobenzaldehyde)]PF_6$ complex, the Ru–S distance (2.314(1) Å) is much shorter than comparable distances in the Ru–mercaptan complexes [25].

The angles about the S atom in **II** are 114.9° for Ru–S–H(S), 95.7° for C(43)–S–H(S) and 110.1(3)° for Ru–S–C(43). The values for the $[CpRu(PPh_3)_2(t\text{-}C_4H_9SH)]BF_4$ complex are 125.7(3), 111.7(1) and 91.9(3)° for the C–S–Ru, Ru–S–H and C–S–H angles, respectively. The C–S–H angle in $[CpRu(PPh_3)_2(n\text{-}C_3H_7SH)]BF_4$ is 99(3)° and the Ru–S–H angle is 97(3)° [17]. For $Cr(CO)_5$(t-butylSH), the Cr–S–H angle is 106(1)° and the Cr–S–C angle is 121.3(2)° [22].

The displacement of n-propylthiol from $CpRu(PPh_3)_2(n\text{-}C_3H_7SH)^+$ can be easily achieved by the addition of the sigma donor ligands Cl^-, Br^-, CH_3CN and dimethyldithiocarbamate. This indicates that the n-propyl mercaptan is weakly coordinated to the ruthenium metal center. Attempts to deprotonate the coordinated mercaptan with BH_4^- lead to the hydride complex and some intractable materials. Further studies of the reactivity of the coordinated mercaptans are under way.

Supplementary material

A listing of general temperature factor expressions (*U*), hydrogen atom coordinates, bond distances and angles (7 pages) and tables of calculated and observed structure factors (42 pages) are available from the authors upon request.

Acknowledgement

Funding provided by the A.S.U. Faculty Research Committee and Competitive Applied Research Grant.

References

1 J. Oudar, in E. E. Petersen and T. A. Bell (eds.), *Catalyst Deactivation*, Marcel Dekker, New York, 1987.
2 L. L. Hegedus and R. W. McCabe, *Catalyst Poisoning*, Marcel Dekker, New York, 1984.
3 J. B. McKinley, *Catalysis V*, Rheinhold, New York, 1957, p. 405.
4 B. C. Gates, J. R. Katzer and G. C. A. Schuit, *Chemistry of Catalytic Processes*, McGraw-Hill, New York, 1979.
5 E. G. Derouane, E. Pedersen, B. S. Clausen, Z. Gabelica, R. Candia and H. Topsoe, *J. Catal., 99* (1986) 253.
6 J. T. Roberts and C. M. Friend, *J. Am. Chem. Soc., 108* (1986) 7204.
7 R. J. Angelici, *Acc. Chem. Res., 21* (1988) 387.
8 R. J. Angelici, *Coord. Chem. Rev., 105* (1990) 61.
9 T. B. Rauchfuss, *Prog. Inorg. Chem., 39* (1991) 259.
10 C. G. Kuehn and H. Taube, *J. Am. Chem. Soc., 98* (1976) 689.
11 T. A. Pecoraro and R. R. Chianelli, *J. Catal., 67* (1981) 430.
12 R. R. Chianelli, T. A. Pecoraro, T. R. Halbert, W.-H. Pan and E. I. Stiefel, *J. Catal., 86* (1984) 226.
13 S. Harris and R. R. Chianelli, *J. Catal., 86* (1984) 400.
14 M. Draganjac, C. J. Ruffing and T. B. Rauchfuss, *Organometallics, 4* (1985) 1909.
15 J. Amarasekera, T. B. Rauchfuss and A. L. Rheingold, *Inorg. Chem., 26* (1987) 2017.
16 J. Amarasekera, T. B. Rauchfuss and S. R. Wilson, *Inorg. Chem., 26* (1987) 3328.
17 J. Amarasekera and T. B. Rauchfuss, *Inorg. Chem., 28* (1989) 3875.
18 G. S. Ashby, M. I. Bruce, I. B. Tomkins and R. C. Wallis, *Aust. J. Chem., 32* (1979) 1003.
19 D. T. Cromer and J. T. Waber, *International Tables for X-ray Crystallography*, Vol. IV, Kynoch, Birmingham, UK, 1974, Table 2.2 A.
20 J. A. Ibers and W. C. Hamilton, *Acta Crystallogr., 17* (1964) 781.
21 D. T. Cromer, *International Tables for X-ray Crystallography*, Vol. IV, Kynoch, Birmingham, UK, 1974, Table 2.3.1.
22 M. Y. Darensbourg, E. M. Longridge, V. Payne, J. Reibenspies, C. G. Riordan, J. J. Springs and J. C. Calabrese, *Inorg. Chem., 29* (1990) 2721.
23 F. M. Conroy-Lewis and S. J. Simpson, *J. Chem. Soc., Chem. Commun.*, (1991) 388.
24 P. M. Treichel and L. D. Rosenhein, *Inorg. Chem., 20* (1981) 942.
25 W. A. Schenk, T. Stur and E. Dombrowski, *Inorg. Chem., 31* (1992) 723.