Short Communication

Oxorhenium(V) complexes with *N*-(thiocarbamoyl)benzamidinates, R$_2$tcb$^-$. X-ray structure of [ReO(et$_2$tcb)$_2$](BPh$_4$)·Ph$_3$PO

Ulrich Abram* and Rainer Hübener
*University of Tübingen, Institute of Inorganic Chemistry, Auf der Morgenstelle 18, W-7400 Tübingen (Germany)*

Abstract

Novel cationic rhenium(V) complexes with *N*-(thiocarbamoyl)-benzamidinato ligands (R$_2$tcb$^-$) with the general formula [ReO(R$_2$tcb)$_2$](BPh$_4$) have been prepared and characterized by elemental analysis, IR and NMR spectroscopy and mass spectrometry. The complexes are brown powders; crystalline products can only be obtained in the presence of triphenylphosphine oxide. [ReO(et$_2$tcb)$_2$](BPh$_4$)·OPPh$_3$ has been studied with X-ray diffraction. The compound crystallizes triclinic in the space group $P\bar{1}$ with $a = 9.771(1)$, $b = 16.886(1)$, $c = 17.731(1)$ Å, $\alpha = 108.91(1)$, $\beta = 95.35(1)$, $\gamma = 104.36(1)°$, $V = 2930$ Å^3 and $Z = 2$. The Re=O bond is 1.663(4) Å. The co-crystallization with tripenylphosphine oxide can be understood with the formation of hydrogen bonds between the NH protons of the chelate and the O atom of Ph$_3$PO.

Introduction

Recently, we reported the synthesis and characterization of oxo and nitrido technetium(V) complexes with *N*-(*N,N*-dialkylthiocarbamoyl)benzamidines, HR$_2$tcb (I) [1, 2] (Het$_2$tcb: R = ethyl; Hmorphtcb; RNR = *N*-morpholinyl; Hpiptcb: RNR = *N*-piperidinyl). The ligands coordinate bidentately with single deprotonation of the NH$_2$ group via the N and S donors [1–3].

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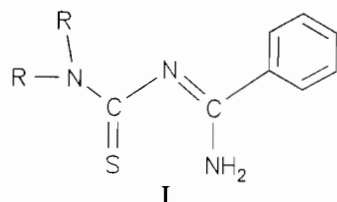
*Author to whom correspondence should be addressed.

Crystalline oxotechnetium complexes of general formula [TcO(R$_2$tcb)$_2$]$^+$ could only be obtained with Cl$^-$ as counterion. An X-ray structure of [TcO(et$_2$tcb)$_2$]Cl suggests the possible formation of a hydrogen bond between the NH protons and the Cl$^-$ to be responsible for this result [1].

Here, we discuss the formation and the structure of oxorhenium(V) complexes with the same type of ligands, together with the crystal and molecular structure determination of [ReO(et$_2$tcb)$_2$](BPh$_4$)·OPPh$_3$.

Experimental

Synthesis

[ReO(et$_2$tcb)$_2$](BPh$_4$)

85 mg (0.1 mmol)ReOCl$_3$(Ph$_3$P)$_2$ were suspended in 50 ml EtOH/CHCl$_3$ (1:1 vol./vol) and 110 mg (2.1 mmol) Het$_2$tcb were added in 10 ml EtOH. The mixture was refluxed for 3 h to yield a clear solution and the solvent was removed in vacuum. The oily residue was washed with ether and dissolved in EtOH. Addition of excess NaBPh$_4$ in EtOH lead to the formation of a yellow–brown precipitate. After reprecipitation from CH$_2$Cl$_2$/EtOH a brown powder was formed which is easily soluble in CH$_2$Cl$_2$, CHCl$_3$, acetone and acetonitrile, only slightly soluble in alcohols and insoluble in hydrocarbons. Yield 69 mg (70% based on Re). *Anal.* Calc. for C$_{48}$H$_{52}$N$_6$OS$_2$BRe: C, 58.2; H, 5.3; N, 8.5; S, 6.5. Found: C, 59.3; H, 5.5; N, 8.0; S, 6.4%. ^{1}H NMR: phenyl: 7.3–7.7m (30H), CH$_2$: 4.07–4.25m (8H), CH$_3$: 1.48tr (6H), 1.42tr (6H). FAB-MS: $m/z = 671$ [M]$^+$, $m/z = 469$ [ReO(et$_2$tcb)S]$^+$, $m/z = 437$ [ReO(et$_2$tcb)]$^+$, $m/z = 365$ [ReO(et$_2$tcb), $-$et$_2$N]$^+$, $m/z = 307$ [ReO(et$_2$tcb), $-$et$_2$NSCN]$^+$. IR: ν(Re=O) = 965(m) cm^{-1}.

[ReO(piptcb)$_2$](BPh$_4$)

The compound was prepared as outlined above for [ReO(et$_2$tcb)$_2$](BPh$_4$). Yield 87 mg (85% based on Re). *Anal.* Calc. for C$_{50}$H$_{52}$N$_6$OS$_2$BRe: C, 59.2; H, 5.3; N, 8.3; S, 6.3. Found: C, 58.1; H, 4.7; N, 7.9; S, 6.0%. ^{1}H NMR: phenyl: 7.3–7.6m (30H), C–CH$_2$–C: 4.12–4.33m (12H), N–CH$_2$: 1.71–1.85m (8H). FAB-MS: $m/z = 695$ [M]$^+$, $m/z = 679$ [Re(piptcb)$_2$]$^+$, $m/z = 609$ [ReO(piptcb)$_2$, $-$5CH$_2$, $-$O]$^+$, $m/z = 449$ [ReO(piptcb)]$^+$. IR: ν(Re=O) = 970(m) cm^{-1}.

[ReO(morphtcb)$_2$](BPh$_4$)

The compound was prepared as outlined above for [ReO(et$_2$tcb)$_2$](BPh$_4$). Yield 70 mg (65% based on Re).

Anal. Calc. for $C_{48}H_{48}N_6O_3S_2BRe$: C, 56.6; H, 4.7; N, 8.5; S, 6.3. Found: C, 57.2; H, 4.8; N, 8.9; S, 6.8%. ^{1}H NMR: phenyl: 7.3–7.7m (30H), CH_2–O: 4.17 broad (8H), N–CH_2: 3.65 broad (8H). FAB-MS: $m/z = 699$ $[M]^+$, $m/z = 683$ $[Re(morphtcb)_2]^+$, $m/z = 613$ $[ReO-(morphtcb)_2, -morph]^+$, $m/z = 527$ $[ReO(morphtcb)_2, -2morph]^+$, $m/z = 483$ $[ReO(morphtcb)_2, -morphCS, -morph]^+$, $m/z = 451$ $[ReO(morphtcb)]^+$. IR: $\nu(Re=O) = 955(m)$ cm^{-1}.

$[ReO(et_2tcb)_2](BPh_4) \cdot OPPh_3$

Single crystals of the composition $[ReO-(et_2tcb)_2](BPh_4) \cdot OPPh_3$ were obtained by adding an ethanolic solution of $NaBPh_4$ to the crude reaction mixture and standing overnight. Yellow–brown crystals. IR: $\nu(P=O) = 1117(st)$ cm^{-1}.

Physical measurements

The ^{1}H NMR spectra were recorded in $CDCl_3$ solutions on a WP 80 spectrometer (Bruker).

IR measurements were carried out for KBr pellets on a Perkin-Elmer 597 instrument.

FAB mass spectra were recorded on a MAT 701A spectrometer (Finnigan). Xenon was used as primary beam gas. The ion gun was operated at 8 kV and 100 μA (probe temperature: 30 °C). Nitrobenzylalcohol was used as matrix.

X-ray diffraction

X-ray data of $[ReO(et_2tcb)_2](BPh_4) \cdot OPPh_3$ were collected at $T = 185$ K on an automated Enraf-Nonius CAD 4 diffractometer. A crystal of approximate dimensions $0.2 \times 0.2 \times 0.4$ mm was used during the measurements. Throughout the experiment Mo $K\alpha$ radiation was used with a graphite crystal monochromator ($\lambda = 0.7093$ Å). The unit cell was determined from the angular settings of 25 high angle reflections: $a = 9.771(1)$, $b = 16.886(1)$, $c = 17.731(1)$ Å, $\alpha = 108.91(1)$, $\beta = 95.35(1)$, $\gamma = 104.36(1)°$, $V = 2930$ Å^3 with $Z = 2$, $D_x = 1.435$ g cm^{-3}. The space group was found to be triclinic, $P\bar{1}$ (No. 2). Intensity data were collected for 20 546 unique reflections of which 17 670 were observed ($I \geqslant 3\sigma(I)$).

The structure was solved by automated heavy-atom Patterson method and refined by full-matrix least-squares techniques (VAXSDP [4]) to a final $R = 0.035$ and $R_w = 0.048$ for 10 282 observations and 712 variables. All non-hydrogen atoms were refined with anisotropic temperature factors. Empirical absorption correction (DIFABS) was applied. The maximum shift over e.s.d. ratio in the last full-matrix least-square cycle was less than 0.0003. The final Fourier map showed maximum peaks of 1.205 e/Å^3. Table 1 contains the fractional positional parameters.

Programs used: VAXSDP, SCHAKAL [5].

TABLE 1. Positional parameters for $[ReO(et_2tcb)_2](BPh_4) \cdot OPPh_3$

Atom	x	y	z	B(Å^2)
Re	0.24784(3)	0.01534(1)	0.03713(1)	2.556(4)
S1	0.3465(2)	−0.09975(9)	0.00377(8)	3.22(3)
S2	0.2387(2)	−0.0067(1)	−0.08517(8)	3.36(3)
O	0.0812(5)	−0.0250(3)	0.0477(2)	4.0(1)
N1	0.3754(5)	0.0612(3)	0.1358(2)	3.0(1)
N2	0.4394(5)	−0.0615(3)	0.1493(3)	3.0(1)
N3	0.3573(6)	−0.2042(3)	0.0783(3)	3.5(1)
N4	0.2868(5)	0.1451(3)	0.0584(3)	3.0(1)
N5	0.2298(5)	0.1610(3)	−0.0551(3)	3.1(1)
N6	0.1063(6)	0.0632(3)	−0.1642(3)	3.8(1)
C1	0.4454(6)	0.0217(4)	0.1698(3)	2.9(1)
C2	0.3818(6)	−0.1216(4)	0.0832(3)	3.0(1)
C3	0.2824(6)	0.1901(4)	0.0148(3)	3.0(1)
C4	0.1868(7)	0.0788(4)	−0.1008(3)	3.2(1)
C11	0.5353(6)	0.0771(4)	0.2432(3)	3.1(1)
C12	0.6244(7)	0.1617(4)	0.2542(4)	3.9(2)
C13	0.7104(8)	0.2141(5)	0.3231(4)	5.0(2)
C14	0.7028(8)	0.1818(5)	0.3793(4)	5.3(2)
C15	0.6137(8)	0.0978(5)	0.3679(4)	5.2(2)
C16	0.5308(7)	0.0438(4)	0.2991(3)	4.0(2)
C21	0.3847(8)	−0.2263(4)	0.1434(3)	3.9(1)
C22	0.5281(9)	−0.2414(6)	0.1531(5)	7.6(2)
C31	0.2940(9)	−0.2799(4)	0.0089(4)	4.8(2)
C32	0.132(1)	−0.3138(6)	0.0009(5)	6.5(3)
C41	0.3413(7)	0.2892(4)	0.0472(3)	3.4(1)
C42	0.4511(8)	0.3299(4)	0.1088(4)	4.4(2)
C43	0.509(1)	0.4219(5)	0.1351(4)	5.7(2)
C44	0.457(1)	0.4704(5)	0.1007(5)	6.0(2)
C45	0.348(1)	0.4285(5)	0.0388(5)	5.7(2)
C46	0.2905(8)	0.3386(4)	0.0124(4)	4.5(2)
C51	0.0717(8)	0.1349(4)	−0.1819(3)	3.9(2)
C52	−0.0620(9)	0.1512(6)	−0.1541(5)	5.9(2)
C61	0.028(1)	−0.0259(5)	−0.2174(4)	5.8(2)
C62	0.093(1)	−0.0456(6)	−0.2832(6)	7.2(3)
P	0.3088(2)	0.29599(9)	0.27731(8)	2.94(3)
O2	0.3466(5)	0.2251(3)	0.2213(2)	3.7(1)
C71	0.4617(7)	0.3916(4)	0.3178(3)	3.1(1)
C72	0.5912(7)	0.3895(4)	0.2935(3)	3.6(1)
C73	0.7135(7)	0.4620(5)	0.3239(4)	4.1(2)
C74	0.7078(7)	0.5361(4)	0.3791(4)	4.0(2)
C75	0.5804(8)	0.5377(4)	0.4055(4)	4.2(2)
C76	0.4569(7)	0.4654(4)	0.3754(4)	3.9(2)
C81	0.1600(7)	0.3229(4)	0.2391(3)	3.1(1)
C82	0.1517(7)	0.4063(4)	0.2525(4)	4.2(2)
C83	0.0253(8)	0.4180(4)	0.2232(4)	4.6(2)
C84	−0.0907(8)	0.3477(5)	0.1826(4)	4.4(2)
C85	−0.0809(9)	0.2636(5)	0.1684(5)	5.6(2)
C86	0.0437(9)	0.2518(4)	0.1954(4)	5.0(2)
C91	0.2527(7)	0.2654(4)	0.3520(3)	3.2(1)
C92	0.1520(7)	0.2983(4)	0.3896(4)	4.0(2)
C93	0.1198(8)	0.2774(5)	0.4500(4)	4.7(2)
C94	0.1869(9)	0.2254(5)	0.4730(4)	5.2(2)
C95	0.2865(8)	0.1927(5)	0.4355(4)	5.1(2)
C96	0.3183(8)	0.2120(4)	0.3747(4)	4.1(2)
C101	0.2127(6)	0.8109(4)	0.3766(3)	2.9(1)
C102	0.2186(7)	0.8700(4)	0.3409(3)	3.6(1)
C103	0.1842(8)	0.9477(4)	0.3709(4)	4.3(2)
C104	0.1405(8)	0.9668(4)	0.4373(4)	4.4(2)
C105	0.1300(7)	0.9085(4)	0.4727(4)	4.2(2)

(continued)

TABLE 1. (continued)

Atom	x	y	z	$B(\text{Å}^2)$
C106	0.1663(7)	0.8318(4)	0.4425(3)	3.6(1)
C111	0.1560(7)	0.6656(4)	0.2595(3)	3.1(1)
C112	0.0113(8)	0.6657(4)	0.2486(4)	4.4(2)
C113	−0.0849(9)	0.6173(5)	0.1830(4)	5.2(2)
C114	−0.040(1)	0.5661(5)	0.1253(4)	5.2(2)
C115	0.1003(9)	0.5638(5)	0.1329(4)	5.1(2)
C116	0.1956(8)	0.6123(4)	0.1994(3)	4.0(2)
C121	0.2377(6)	0.6626(4)	0.3924(3)	2.9(1)
C122	0.1093(7)	0.5985(4)	0.3849(4)	4.0(2)
C123	0.0898(8)	0.5491(5)	0.4293(4)	4.8(2)
C124	0.1983(8)	0.5636(4)	0.4849(4)	4.5(2)
C125	0.3287(7)	0.6288(4)	0.4957(3)	4.0(2)
C126	0.3455(7)	0.6763(4)	0.4501(3)	3.5(1)
C131	0.4344(6)	0.7478(4)	0.3354(3)	3.1(1)
C132	0.5258(7)	0.8349(4)	0.3586(4)	4.0(2)
C133	0.6736(8)	0.8558(5)	0.3592(4)	4.8(2)
C134	0.7381(8)	0.7897(5)	0.3362(4)	4.7(2)
C135	0.6527(7)	0.7035(4)	0.3141(4)	4.4(2)
C136	0.5043(7)	0.6830(4)	0.3138(3)	3.7(1)
B	0.2611(7)	0.7217(4)	0.3401(4)	2.9(1)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)\cdot[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc(\cos\alpha)B(2,3)]$.

Results and discussion

Cationic oxorhenium(V) complexes with *N*-(*N,N*-dialkylthiocarbamoyl)benzamidines (**I**) can be obtained by a ligand exchange procedure starting from ReOCl₃(Ph₃P)₂. The products can be isolated as tetraphenylborate salts which are easily soluble in polar organic solvents such as acetone, acetonitrile or CHCl₃. The chelating ligands coordinate via sulfur and nitrogen donors by single deprotonation. IR bands due to the $\nu_{(Re=O)}$ vibrations can be observed between 955 and 970 cm^{-1}.

The complexes are diamagnetic as expected for d² complexes with a central oxo (or nitrido) group [6, 7]. ¹H NMR spectra show no significant changes in the spectral parameters with respect to the spectra of the non-coordinated ligands [1] with the exception of the NH protons, the NMR signals of which could not be assigned unambiguously in the spectra of the complexes under study.

FAB⁺ mass spectra confirm the structure of the [ReO(R₂tcb)₂]⁺ cations. Intense peaks could be observed due to the molecular ions. The molecular ion region of the [ReO(piptcb)₂]⁺ spectrum is shown in Fig. 1. Typical isotopic patterns can be found for the rhenium containing fragments (¹⁸⁷Re: 62.60% and ¹⁸⁵Re: 37.40% natural abundance). Beside the peak at $m/z = 695$ which is evident from the molecular ion, a number of metal containing fragments can be found.
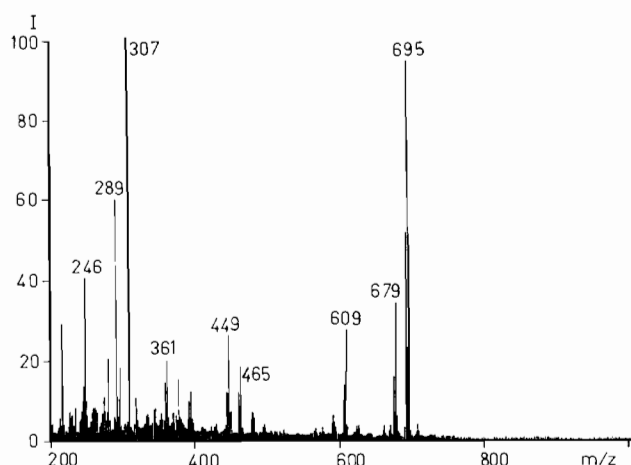

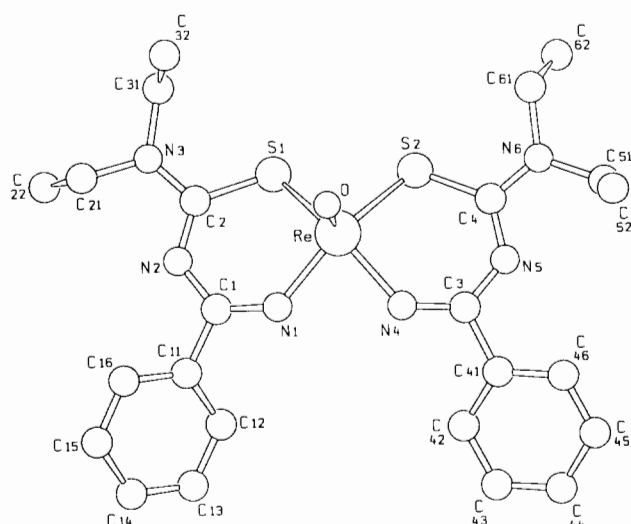Fig. 1. High mass region of the FAB⁺ mass spectrum of [ReO(piptcb)₂](BPh₄).

Fig. 2. SCHAKAL plot of the cation [ReO(et₂tcb)₂]⁺ along with the atomic numbering scheme.

They are caused by loss of oxygen ($m/z = 679$) and sulfur ($m/z = 663$). Other principal fragments appear from the additional loss of a complete ligand and/or ligand fragments. The general fragmentation patterns of the rhenium complexes under study come very close to those of the analogous technetium compounds which are extensively studied by mass spectrometry also including MIKE spectra [1, 8]. The oxo ligands are generally included into the mass spectrometric fragmentation.

Crystals suitable for X-ray diffraction could only be obtained from the mother liquid of the reaction mixture. The crystals contain one molecule triphenylphosphine oxide per unit [ReO(R₂tcb)₂](BPh₄). The molecular structure of the complex cation along with the atomic numbering scheme is given in Fig. 2. Table 2 contains selected interatomic distances and angles. The rhenium

TABLE 2. Selected bond lengths and angles in $[ReO(R_2tcb)_2]^+$

Bond lengths (Å)					
Re–O	1.663(4)	S1–C2	1.748(7)	S2–C4	1.748(8)
Re–S1	2.315(2)	C2–N2	1.330(6)	C4–N5	1.322(7)
Re–S2	2.309(2)	C1–N2	1.314(8)	C3–N5	1.309(7)
Re–N1	2.008(4)	C1–N1	1.341(9)	C3–N4	1.323(9)
Re–N4	2.020(5)	C2–N3	1.325(9)	C4–N6	1.325(9)
Bond angles (°)					
O–Re–S1	107.2(2)		Re–N1–C1		131.1(3)
O–Re–S2	107.4(2)		Re–S2–C4		107.5(3)
O–Re–N1	107.0(3)		Re–N4–C3		131.7(3)
O–Re–N4	108.7(2)		S1–Re–N1		88.5(2)
S1–Re–S2	80.5(1)		S1–Re–N4		144.1(4)
N1–Re–N4	81.0(2)		S2–Re–N4		89.1(1)
Re–S1–C2	105.2(2)		S2–Re–N1		145.6(2)

is five-coordinate with the oxo ligand at the apex of a distorted square pyramid. The basal plane of this pyramid is formed by the nitrogen and sulfur donor atoms of the organic ligands. The Re atom lies 0.6491(1) Å out of this plane towards the 'O^{2-}' ligand. In accordance with other rhenium monooxo complexes [9] the Re=O distance was found to be 1.663(4) Å. The et_2tcb^- ligands are in a *cis* arrangement with respect to their donor atoms S and N. This is the same bonding feature as was found for $[TcO(et_2tcb)_2]^+$ [1] and contrasts with the situation in the nickel chelate $Ni(et_2tcb)_2$, where a *trans* coordination was observed [10]. The interligand S–S distance is 2.988(3) Å in $[ReO(et_2tcb)_2]^+$ and thus a weak interaction between the sulfur atoms may be discussed to be responsible for the *cis* coordination as was done for copper(II) and nickel(II) complexes with monothio-β-diketonates and benzoylthioureas [11].

In contrast to the situation in $[TcO(et_2tcb)_2]^+$, where almost equal bond lengths were found for the C–N bonds in the chelate ring systems, the title compound shows distinct distances for the C1–N1 and C3–N5 bonds with considerable double bond character (1.311(3) Å) and the C1–N1, C2–N2, N4–C3 and N5–C4 distances (1.323–1.341 Å), respectively. The C–S bond lengths correspond to values lying between single- and double-bond character.

It is interesting to note that $[ReO(et_2tcb)_2](BPh_4)$ only crystallizes in the presence of triphenylphosphine oxide. This can be discussed in terms of a weak interaction of $OPPh_3$ and the complex cation. The oxygen atom of $OPPh_3$ is strictly oriented towards the nitrogen donor site of the complex cation as illustrated by the crystal packing plot in Fig. 3. Intermolecular distances of 2.834(6) and 2.991(6) Å between the O atom in $OPPh_3$ and N1 and N2, respectively, suggest the formation of hydrogen bonds with the H atom of the only singly-deprotonated NH_2 function of the ligand. This assumption is supported by the IR frequency of the
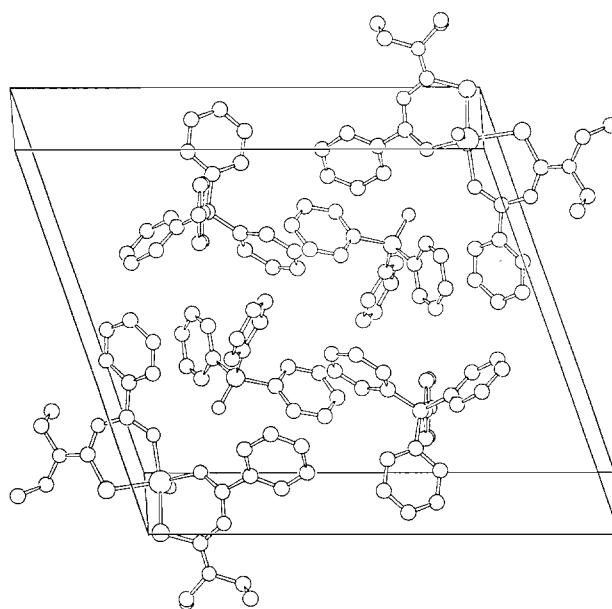
Fig. 3. Unit cell packing of $[ReO(et_2tcb)_2](BPh_4)\cdot OPPh_3$.

NH bond at $3210\ cm^{-1}$ in $[ReO(et_2tcb)_2](BPh_4)\cdot OPPh_3$ which shows a considerable shift with respect to the values in the non-coordinated ligand (3320, 3420 cm^{-1}) and in the mixed-ligand rhenium(V) complex $[ReN(Cl)(et_2tcb)(Me_2PhP)_2]$ (3318 cm^{-1}) [12].

Supplementary material

Further details of the crystal structure determination have been deposited with the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, as Supplementary Publication No. CSD 56575.

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