ROBL-CRG	**Experiment title:** EXAFS Analysis of a Rhenium(I) Carbonyl Complex	**Experiment number**: 20_01_02
Beamline: BM 20	**Date of experiment**: from: 27/01/99 to: 03/02/99	**Date of report**: 24/08/99
Shifts: 21	**Local contact(s)**: Tobias Reich	*Received at ROBL:* 26.8.99

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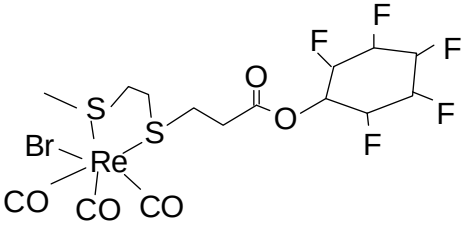
Report:

First EXAFS measurements of a rhenium(I) carbonyl complex were performed using the Rossendorf Beamline (ROBL). Being a collaboration between the Institute of Radiochemistry and the Institute of Bioinorganic and Radio-pharmaceutical Chemistry, this analysis serves as a stepping stone towards preparing future EXAFS experiments with ^{99}Tc carbonyl complexes.
Rhenium and technetium carbonyl complexes of the general formula $[M(CO)_3XL]$ (M = Re, Tc; X = Br^-, Cl^-; L = bidentate thioether or Schiff base ligand) are at present under study for the development of neutral receptor-affine complexes which are able to cross the blood-brain barrier and to bind to receptors of the central nervous system. Some of the rhenium carbonyl thioether complexes are fully characterized by X-ray analysis and other chemical methods, whose data may be used for comparison with EXAFS results.

The EXAFS spectra of the Re L_{III} and Br K-edges of the same sample were measured in transmission mode, using the Si(111) double-crystal monochromator in fixed-exit mode.
The sample consists of 20 mg of the following rhenium complex:



mixed with Teflon powder as matrix material and pressed into a pellet. The EXAFS spectra were evaluated, using the program package EXAFSPAK, and the scattering code FEFF6.
To obtain a satisfactory fit result for the Re spectra, the individual scattering paths Re-C, Re-S, and Re-Br and the multiple scattering path along the carbonyl group, i.e. Re-C-O, have to be included (see Tab. 1).

The EXAFS scan of the same compound with bromine as the central atom gives a more complicated spectrum, which is dominated by the heaviest possible backscatterer rhenium. Apart from the main scattering path Br – Re, the nearly linear multiple scattering paths Br – Re – C and Br – Re – C – O yield the most important contributions to the radial distribution function. The evaluated bond length Br – Re is 2.60 Å**.**

Tab. 1 Comparison of bond distances obtained by EXAFS measurement and X-ray analysis data (XRD) of similar complexes ($\Delta R_{EXAFS} < 0.02$ Å**)**

	EXAFS			XRD [1]	XRD [2]
Path	N	σ^2 [3]	R [Å]	R [Å]	R [Å]
Re – C1 Re – C2 Re – C3	2.7	1.8	1.92	1.92 1.90 1.90	1.98 1.94 1.92
Re – Br	0.9	3.3	2.62	2.64	2.61
Re – S1 Re – S2	2.4	3.6	2.49	2.47 2.46	2.54 2.53
Re-C-O (3 legs)	2.7[4]	3.0	3.07	3.07	no data
Re-C-O (4 legs)	2.7	3.0	3.06	3.07	

[1] $Re(CO)_3Br(CH_3\text{-}S\text{-}C_2H_4\text{-}S\text{-}CH_3\text{-}CCH)$, (2)
[2] $Re(CO)_3Br(Cl\text{-}C_2H_4\text{-}S\text{-}C_2H_4\text{-}S\text{-}C_2H_4\text{-}Cl)$, (3)
[3] Debye Waller factors in 10^{-3} Å^2
[4] The degeneracy of 2 was taken into account

Measurements of the inner coordination spheres of rhenium carbonyl complexes which differ in dithioether ligands using X-ray crystal structure methods, lead to Re – Br distances between 2.61 and 2.64 Å (1,2). The presented EXAFS results are consistent with these data.

References

(1) Reisgys M. (1998) Rhenium- und Technetiumkomplexe mit Thioetherliganden, *Thesis*, TU Dresden
(2) Alberto R., Schibli R., Angst D., Schubiger P. A., Abram U., Abram S. and Kaden Th. A. (1997) Application of technetium and rhenium carbonyl chemistry to nuclear medicine, *Transition Met. Chem.* **22**, 597-601.