Polish J. Chem., **76**, 285–293 (2002)

Crystal Structure, EXAFS Study and Low Temperature Magnetic Properties of Ammonium Hexabromorhenate*

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(Received June 18th, 2001; revised manuscript September 24th, 2001)

Crystal and molecular structures of ammonium hexabromorhenate $(NH_4)_2ReBr_6$ have been determined by the heavy atom method. The title compound crystallizes red-violet crystals in the space group $Fm\bar{3}m$ with $Z = 4$. The Re atom is of six-coordinate octahedral configuration, being bonded to six bromide anions. The magnetic behaviour of $(NH_4)_2ReBr_6$ has been investigated over the temperature range 1.72–300 K. These measurements revealed that this compound is an antiferromagnet with Neél temperature T_N = 15.5 K. The magnetic data are interpreted in terms of zero-field splitting of the ground $^4A_{2g}$ term (D = 22.8 cm^{-1}), large because of the high spin-orbit coupling constant for the Re^{+4} ion, with antiferromagnetic exchange coupling (J = –17.7 cm^{-1}).

Key words: rhenium complexes, magnetism, crystal structure, FIR spectra, EXAFS

The search for new materials showing useful magnetic or magneto-optical properties is one of the main goals of molecular magnetism [1]. It is related to both molecular and solid state physics and involves synthetic chemistry and theoretical chemistry. To design molecular systems with expected magnetic behaviour, it is necessary to use a quite original compound containing several kinds of metallic ions, organic ligands and novel bridging networks. For this synthesis a very important role play the strategies that derive from an understanding of the underlying mechanism of the phenomena. For example, the spin transition phenomenon, that occurs in some transition metal complexes, is a spectacular example of molecular bistability. This kind of molecular magnets are used in the emerging field of molecular electronics, *i.e.* in applications of molecular materials in electronic circuits [2].

In molecular magnetism we can specify two kinds of scope: molecular magnetism of isolated molecules and assemblies of molecules. These molecules may contain one or more magnetic centers. Assemblies of molecules are most often found in a molecular crystal with very weak interactions between the molecular entities. They can also be built by molecular precursors, specially chosen to achieve a 3D covalent

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*Dedicated to the memory of Professor Krzysztof Pigoń.

bonding network between spin-bearing species [3]. One of the simplest and most convenient molecular building block is found in the hexacyanometallate family, $[B(CN)_6]^{n-}$. When $[B(CN)_6]^{n-}$ reads with labile $[A(H_2O)_6]$ assembling ions, tridimensional systems result, which are analogs of the Prussian blue family. These molecular materials are characterized by a higher spin and higher ground state anisotropy and T_c around room temperature.

However, up-to-now the design of a new magnetic precursor has been generally restricted to metal ions belonging to the first transition series. The magnetic behaviour of second- and third-transition series complexes is far less known than that of the first series [2]. Meantime, the larger spin-orbit coupling effects and greater covalence in such compounds may produce an interesting magnetic behaviour [4]. This is the case of rhenium(IV) complexes.

Re(IV), $5d^3$ ion forms usually octahedral complexes, which are reasonably stable against redox processes and inert to ligand substitution [5]. Numerous species in the class of octahedral hexachloro-, haxabromo- and hexaiodorhenate compounds were studied with some details [6–8]. Magnetic measurements indicated a strong increase of magnetic coupling of rhenium(IV) centers in the series M_2ReCl_6, M_2ReBr_6, M_2ReI_6. This antiferromagnetic interaction depends on the halogen-halogen separation between ions in the solid. The magnetic exchange is relatively strong in potassium salts and very weak when using bulky organic cations. Only for some Re(IV) complexes of this series the crystal structures were determined. We succeeded in determination of the crystal structure of molecular precursor of $(NH_4)_2ReBr_6$ and consequently this compound was studied by spectroscopic and variable-temperature magnetic measurements.

EXPERIMENTAL

Materials: Ammonium perrhenate(VII), ammonium iodide, hydroiodic acid, hydrobromic acid.

Synthesis: $(NH_4)_2ReBr_6$ was synthesized by heating a solution of ammonium perrhenate, ammonium iodide and 5 ml of hydroiodic acid in concentrated hydrobromic acid for 4 hours. After cooling, red-violet crystals settled down. The precipitate was next recrystallized from the concentrated hydrobromic acid and repeatedly washed with chloroform and ether [9]. Yield 65 –75%. Anal. Calcd. for $(NH_4)_2ReBr_6$: H,1.14 ; N, 3.99; Br, 68.3%. Found: H, 1.13; N, 3.92; Br, 68.1%. The rhenium content was determined by ICP method. Re (calcd.): 26.5%; Re (found): 26.4%.

Reagents and apparatus: Far infrared (FIR) spectra (400–100 cm^{-1}) in Nujol film were recorded with a Perkin-Elmer Model 180 spectrophotometer.

Crystal structure determination and refinement: The crystal structure of $(NH_4)_2ReBr_6$ was solved by direct methods and full-matrix least-squares refinement to R1 = 0.0258 and wR2 = 0.0650. The hydrogen position is derived from difference Fourier maps (further information: Table 1).

X-ray absorption study: EXAFS measurements have been performed on the XAS 13 beam line of the DCl storage ring (1.85 GeV, positron current = 300 mA) at LURE in Orsay. Incident beam was monochromatized using a Si 111 double crystal. The energy calibration was checked using a Pt foil (L_{III} edge = 11564 eV). EXAFS spectra were recorded at the Re L_{III} edge (10534 eV) in transmission mode using argon filled ionization chambers. Each spectrum was acquired four times under the same experimental conditions (sampling step, 2 eV with an integration time of 2.0s per point). The samples were ground and homogeneously dispersed in cellulose pellets. The EXAFS signal χ (k) expressed as a function of the wave – vector k of the photoelectron is related to the sum of sinusoidal oscillations for each shell of neighbours around the absorbing atom [10]. The EXAFS data analysis is performed with the "EXAFS pour le Mac" package [11]. The EXAFS signal kχ(k) is extracted from the data by a linear preedge background, a combination of polynomials and spline atomic absorption background and the normalization procedure of Lengeler-Eisenberger [12]. The FT are presented without phase correction. In the framework of single scattering approximation, the EXAFS signals are fitted with the ROUND MIDNIGHT programme. We use the FEFF7 code [13] to calculate multiple scattering events (DM), when they are supposed to be present in the EXAFS signal.

Table 1. Crystal data and structure refinement for $(NH_4)_2ReBr_6$.

Identification code	Ammonium hexabromorhenate(IV)
Empirical formula	$H_8Br_6N_2Re$
Formula weight	701.74 g/mol
Temperature	150 K
Wavelength	0.71073 Å
Crystal system, space group	cubic, $Fm\overline{3}m$
Unit cell dimension	a = 10.3922(8) Å
Z	4
Calculated density	4.153 Mg/m^3
Volume	1122.34(15) Å^3
Absorption coefficient	32.127 mm^{-1}
F(000)	1228
Crystal size	0.35×2×1 mm
Theta range for data collection	3.40 to 30.40°
Index ranges	–14<=h<=14, –14<=k<=14, –14<=l<=14
Reflections collected/unique	3481/119 [R(int) = 0.0826]
Completeness to 2θ = 30.40	98.3%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	119/1/8
Goodness-of-fit on	F^2 1.172 < 41
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0258, wR2 = 0.0650
R indices (all data)	R1 = 0.0258, wR2 = 0.0650
Extinction coefficient	0.00021(11)
Largest diff. peak and hole	1.387 and –1.729 e.Å^{-3}

Magnetic measurements: Magnetic measurements between 1.79–300 K were determined using a Quantum Design SQUID magnetometer (type MPMS-5). Measurements were made in W. Trzebiatowski Institute for Low Temperature and Structure Research PAS, Wrocław. The SQUID magnetometer was calibrated with palladium rod sample (Materials Research Corporation, measured purity 99.9985%) for which the gram magnetic susceptibility was taken as 5.30×10^{-6} cm^3 g^{-1} at 293 K (National Bureau of Standars, USA) [14]. All susceptibility measurements were made at 5 kGs. The corrections for diamagnetism of the constituent atoms were calculated from the Pascal constants [15].

RESULTS AND DISCUSSION

Description of the structure: $(NH_4)_2ReBr_6$ crystallizes in the cubic space group $Fm\overline{3}m$ with $a = 10.3928\ (8)$ Å, $V = 1122.3\ (1)$ Å^3, $Z = 4$. The arrangement of the ammonium cations and hexabromorhenate(IV) anions corresponds to the anti-fluorite type, with Re(IV) on positions of Ca^{2+} and N on those of F^-. Regular $ReBr_6$–octahedra with d(Re-Br) = 2.5063 (8) Å are packed in the manner of a cubic closest packed structure with NH_4^+ cations in the tetrahedral interstices. The shortest distances N–Br and N–H with 3.675(1) and 3.14(1) Å are responsible for the very weak hydrogen bonds (angle N–H····Br = 136°) (Table 2, 3). The numbering scheme of the $(NH_4)_2ReBr_6$ is shown in Figure 1. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D – 76344 Eggenstein-Leopoldshafen, Germany (Fax: (+49)7247-808-666; e-mail:crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-412159.

EXAFS study: We used EXAFS spectroscopy to characterize the local structure in the powder ammonium hexabromorhenate compound by comparison with the known crystal structure. The Fourier transform of the $(NH_4)_2ReBr_6$ exhibits only two peaks (Fig. 2). The first one corresponds to the nearest bromo-neighbours. The best fitted curve of the first shell contribution filtered in the range 1.8–3.2 Å is obtained with six bromo-atoms at 2.48 Å with a Debye-Waller factor 0.07 Å (Fig. 3). All structural parameters are summarized in Table 4. The number of neighbours and the distances obtained for these first shells by quantitative analysis are in good agreement with those found by X-ray diffraction. To assign the origin of the second peaks we used the structural parameters to calculate the EXAFS signals with the FEFF7 code including mul-

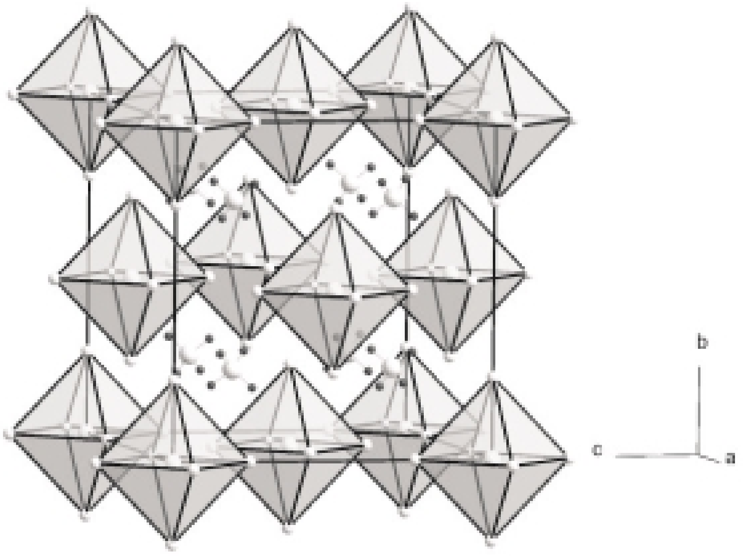

Figure 1. Crystal packing of $(NH_4)_2ReBr_6$.

tiple scattering phenomena [17]. For $(NH_4)_2ReBr_6$, the comparison of the modulus Fourier transforms of the experimental and calculated EXAFS signal with and without multiple scattering shows that the second peak is only due to multiple scattering events in the $ReBr_6^{2-}$ unit (Fig. 4).

Table 2. Atomic coordinates (Å) and equivalent isotropic displacement parameters (Å^2 × 10^3) for $(NH_4)_2ReBr_6$ (U(eq) is defined as one third of the trace of the orthogonalized Uij tensor).

	x	y	z	U(eq)
Re	0.0	0.0	0.0	9(1)
Br	0.0	0.7588(1)	0.0	19(1)
N	0.25	0.75	0.7500	15(2)
H	0.211(4)	0.711(4)	0.789(4)	30 (fixed)

Table 3. Anisotropic displacement parameters (Å^2×10^3) for $(NH_4)_2ReBr_6$. The anisotropic displacement factor exponent takes the form: –2 pi2 [h^2 a*2 U11 + ... + 2 h k a* b* U12].

	U11	U22	U33	U23	U13	U12
Re(1)	9(1)	9(1)	9(1)	0	0	0
Br(2)	24(1)	9(1)	24(1)	0	0	0
N(1)	15(2)	15(2)	15(2)	0	0	0

Magnetic properties: The magnetic properties of $(NH_4)_2ReBr_6$ complex expressed as a plot of $\chi_M T$ *versus* T (χ_M being the molar magnetic susceptibility) are shown in Figure 5. The $\chi_M T$ value rapidly decreases from room temperature and it vanishes at very low temperatures. The susceptibility curves exhibit the maximum at 15.5 K, indicating antiferromagnetic interactions. The magnetic exchange interactions between the Re(IV) cations occur *via* the bromide anions and may be transmit-

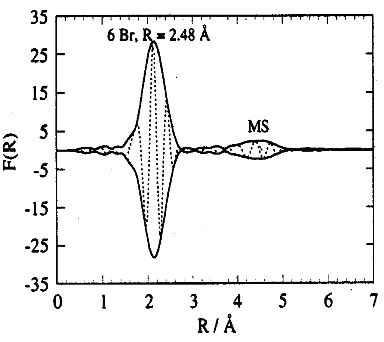

Figure 2. Fourier transforms of EXAFS signal of $(NH_4)_2ReBr_6$.

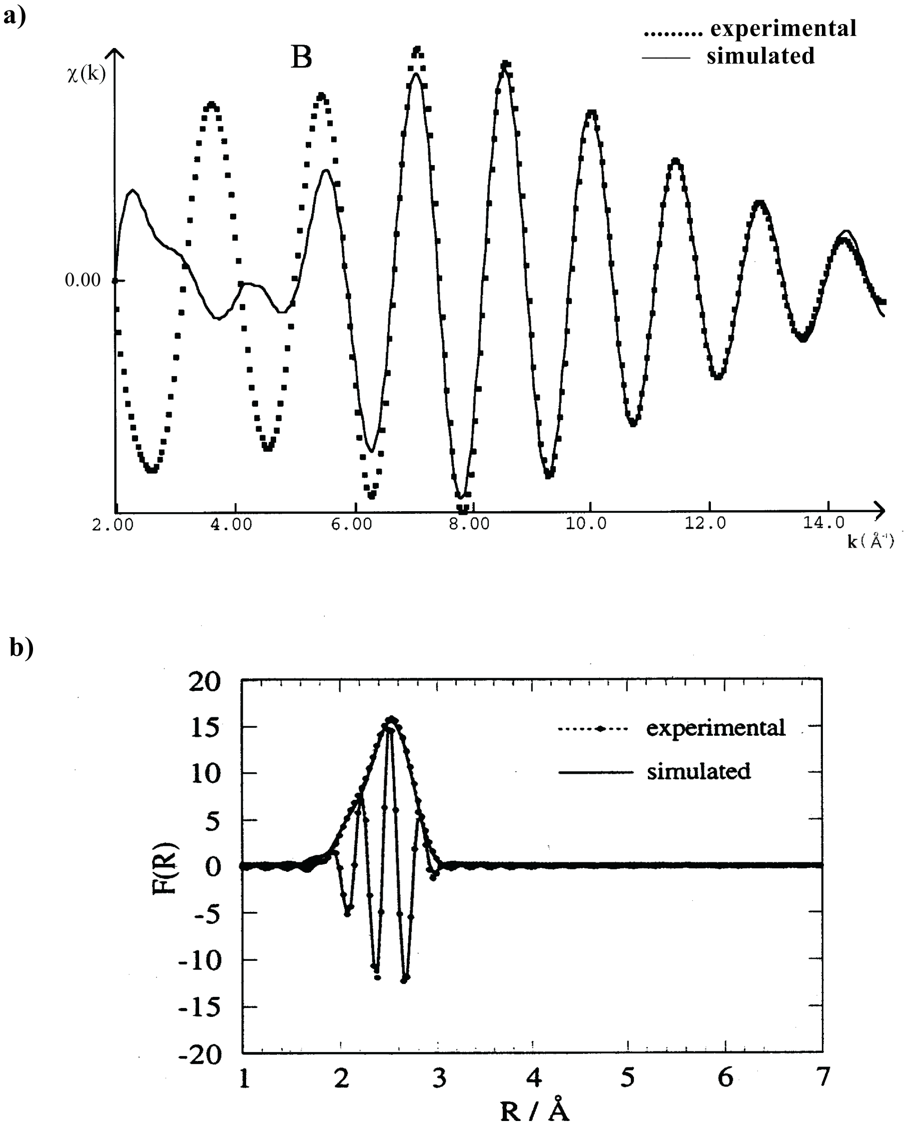

Figure 3. Best fit of the first shell contribution of $(NH_4)_2$ $ReBr_6$: a) in k space; b) in R space.

ted by bonding arrangements, such as M–L---L–M. In the crystal lattice of this compound there appear two types of the exchange interaction, *i.e.* the nearest-neighbours (nn), where the atoms are coplanar and the next-nearest-neighbours (nnn), where the atoms are colinear (Table 5). The magnetic behaviour of this type of mononuclear rhenium(IV) complexes can be understood from the above theoretical point of view.

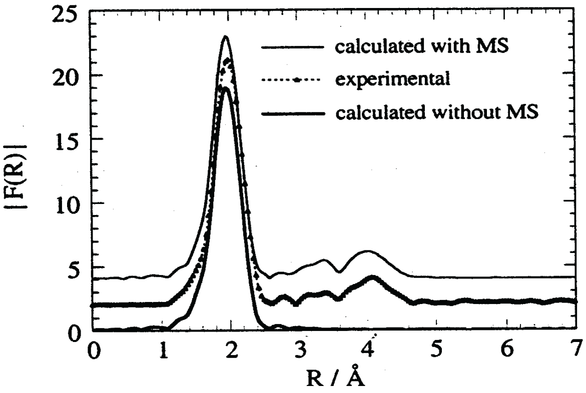

Figure 4. Modulus Fourier transforms of EXAFS signal of $(NH_4)_2\,ReBr_6$, experimental and calculated with and without multiple scattering. The curves are arbitrary shifted to more clearness.

Table 4. Fitted structural parameters of the first shell of neighbours for $(NH_4)_2ReBr_6$.

Backscatterer	Br
N	6
σ (Å)	0.07
Γ	0.8
R (Å)	2.48
E_0 (eV)	10534
ρ (%)	2

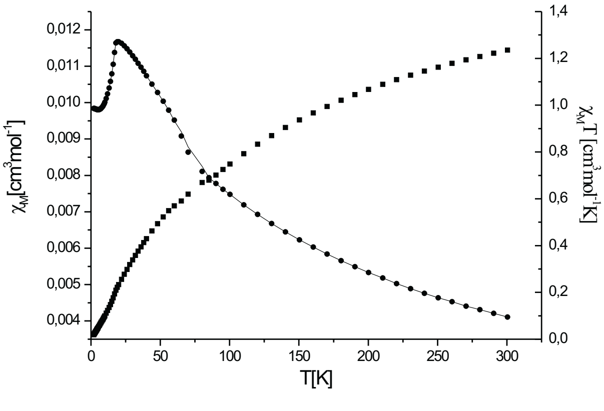

Figure 5. Thermal dependence of χ_M (●) and $\chi_M T$ (■) for $(NH_4)_2ReBr_6$. The solid line are the calculated curve.The value of field is 0.5 T.

Table 5. The distances between atoms in the crystal lattice of $(NH_4)_2ReBr_6$.

Distances	Exchange interaction (nn) [Å]	Exchange interaction (nnn) [Å]
Re--Re	7.38	10.44
Re--Br	2.51	2.51
Br--Br	3.86	5.42
Re-Br····Br-Re	8.84	10.57

Rhenium(IV) with 3 unpaired electrons in an octahedral environment has the electron configuration $(t_{2g})^3$, the ground term is $^4A_{2g}$. The first excited state is $^4T_{2g}$, arising from the ^4F free-ion ground state. The quarted spin ground state, $^4A_{2g}$ is removed by the spin-orbit interaction, leading to two Kramers doublets ±1/2, ±3/2 (zero-field splitting).

If the zero-field splitting parameter, D, is positive, the ground state is composed of ± 1/2 state. The relevant spin Hamiltonian is expressed by

$$H = -2J\sum S_{z,i}S_{z,i+1} + g_{||}\beta H_z S_{z,i} + g_{\perp}\beta(H_x S_{x,i} + H_y S_{y,i}) + D\left(S_z^2 - 1.25\right) \tag{1}$$

The variable-temperature susceptibility data were analyzed using the approach, which consists of the assumption that the susceptibility is given by that of the $^4A_{2g}$ term including zero field splitting parameter [5,18] of the magnetic exchange. The parallel and perpendicular susceptibility are defined by

$$\chi_{||} = \left[\frac{Ng_{||}^2\beta^2}{4kT}\right]\cdot\left[1 + 9\exp\left(\frac{-2D}{kT}\right)\right]\cdot\left[1 + \exp\left(\frac{-2D}{kT}\right)\right]^{-1}\cdot\exp\left(\frac{J}{kT}\right) \tag{2}$$

$$\chi_{\perp} = \left\{\left[\frac{Ng_{\perp}^2\mu_B^2}{kT}\right]\cdot\left[1 + \exp\left(\frac{-2D}{kT}\right)\right]^{-1} + 3Ng_{\perp}^2\mu_B^2\tanh\left(\frac{\mathrm{D}}{\mathrm{kT}}\right)/4D\right\}\cdot$$
$$\left\{\left(\frac{kT}{J}\right)\tanh\left(\frac{J}{2kT}\right) + \left[\mathrm{sec}h^2\left(\frac{J}{2kT}\right)\right]/2\right\} \tag{3}$$

where D is the zero field splitting parameter, N – Avogadro number, g – the spectroscopic splitting factor, β – Bohr magneton, k – Boltzmann constant. The average magnetic susceptibility is equal to:

$$\chi_{av} = \frac{1}{3}\chi_{||} + \frac{2}{3}\chi_{\perp} \tag{4}$$

This equation allows to reproduce theoretically (solid line in Fig. 5) the experimental susceptibility data of $(NH_4)_2ReBr_6$ in the whole temperature range. The best fit parameters are: $D = 22.8$ cm^{-1}, $g_{||} = 1.78$ and $g_{\perp} = 1.69$ and $J = -17.7$ cm^{-1}.

IR spectra: From the six normal modes of vibration of molecules of the type XY_6 [19] only two are infrared active. The octahedral $[ReBr_6]^{2-}$ ion has two deformation bands δ (Br–Re–Br) at 137 cm^{-1} (F_{2g}) and ν (Re–Br) vibrations at about 222 cm^{-1} (F_{1u}).

Acknowledgments

This work was supported by the Polish State Committee for Scientific Research, Grant No 3T09A 03915, and European Science Foundation (ESF/PESC) programm "Molecular Magnets" (MM).

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