Materials Science-Poland, Vol. 22, No. 1, 2004

Synthesis, structure and magnetic susceptibility of ammonium hexaiodorhenate(IV)

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This work reports on the synthesis, magnetic properties and crystal structure of $(NH_4)_2ReI_6$. Bright violet $(NH_4)_2ReI_6$ is tetragonal, $P4/mnc$ (No. 128), $a = b = 7.7436(6)$, $c = 11.6403(14)$ Å, $Z = 2$, $D_x = 4.68$ g/cm^3, $T = 100(1)$ K. The structure was refined to $R = 0.074$ for 438 reflections observed. The anion $[ReI_6]^{2-}$ has an octahedral environment. The temperature dependence of the magnetic susceptibility measured over the range of 4–300 K exhibits the Curie point at 20 K, indicating the presence of antiferromagnetic interaction between the rhenium centres.

Keywords: *rhenium(IV); iodine complex; magnetic susceptibility*

1. Introduction

The magnetic susceptibilities of K_2ReCl_6 and K_2ReBr_6 have been measured over the temperature range of 80–300 K by several authors [1–4]. The effective magnetic moments calculated from the equation $\mu_{\mathrm{eff}} = 2.84[\chi_m(T + \theta)]^{0.5}$ range from 3.6 to 3.8 B.M., compared to 3.87 B.M. for the spin-only moment of three unpaired electrons in the 5d shell. However, the magnetic moment of 3.87 B.M. should not be observed because of a relatively strong spin-orbit coupling exhibited by 5d transition ions. Rhenium salts with antiferromagnetic superexchange can be further used as starting materials for other antiferromagnetic materials. The replacement of I^- ions in the ReI_6^{2-} ion by other doubly (or more) binding ligands may lead to obtaining entirely new Re(IV) complexes with interesting magnetic properties.

The compound under study possesses interesting magnetic properties. In this salt, the occurrence of antiferromagnetic superexchange phenomenon is observed, and it might be useful for obtaining new Re(IV)-based magnetic substances.

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2. Experimental

2.1. Synthesis

$(NH_4)_2ReI_6$ was obtained by a reaction of NH_4ReO_4 with NH_4I in an HI solution, as reported previously [5]. 10 g of ammonium tetraoxorhenate(IV) and 1.2 g of ammonium iodide were heated at 80 °C in 0.5 dm^3 of concentrated hydroiodic acid. The reaction stopped after 21 hours. A change of colour was observed during the reactions, from colourless to yellow, brown, dark brown and the final colour was black. The product was washed separately with $CHCl_3$ (about 2.5–3 dm^3 until the $CHCl_3$ was colourless) and ethyl ether. The elemental analyses of C, H and N matched the theoretical calculations. Preparation of crystals for X-ray measurements is very difficult and only very few of them were found appropriate for X-ray investigations.

2.2. Physical measurements

Magnetic measurements of polycrystalline samples were carried out over the temperature range of 4–300 K using a Quantum Design SQUID-Based Magnetometer MPMSXL5. The measurements were carried out at the Faculty of Chemistry, University of Wrocław, Wrocław, Poland. The SQUID magnetometer was calibrated with a palladium rod sample for which the gram susceptibility was assumed as 5.30×10^{-6} $cm^3\cdot g^{-1}$ at 293 K (National Bureau of Standards, USA). The susceptibility measurements were made in the field of 0.5 T. Corrections were done for the diamagnetic response of the sample rod and of the sample using Pascal's constants [6].

Table 1. Crystallographic data and structure refinement details for $(NH_4)_2ReI_6$

Empirical formula	$H_8N_2I_6Re$	$F(000)$	830
Formula weight	983.68	Crystal size	0.07×0.05×0.05 mm
Temperature	100(1) K	Θ range for data collection	3.72–28.29 deg
Wavelength	0.71073 Å	Index ranges	$-8 \le h \le 10$ $-9 \le k \le 10$ $-15 \le 1 \le 14$
Crystal system	tetragonal	No. of reflections collected	4213
Space group	*P*4/*mnc* (No.128)	No. of independent reflections	438 (R(int) = 0.0739)
Unit cell dimensions	$a = b = 7.7436(6)$ Å $c = 11.6403(14)$ Å	Refinement method	full-matrix least-squares on F^2
Volume	697.99(11) $Å^3$	Goodness-of-fit on F^2	1.05
Z	2	Final R indices $[I > 2(I)]$	$R1 = 0.0739$, $wR2 = 0.1584$
Density (calculated)	4.68 Mg/m^3	R indices (all data)	$R1 = 0.0757$, $wR2 = 0.1589$
Absorption coefficient	9.91 mm^{-1}		

A crystal of approximate dimensions of 0.07×0.05×0.05 mm^3 was used for the data collection. The intensity data were collected at 100(1)K using a CCD detector on a KM4 diffractometer and graphite-monochromated MoKα radiation. The images were indexed, integrated, and scaled using the KUMA CrysAlis [7] data reduction package. The experimental details together with crystal data are given in Table 1. The structure was solved by heavy atom methods using SHELXS97 [8] and refined by least-squares minimization of $\sum w(F_0^2 - F_c^0)^2$ for all reflections [9]. The Re, I and N atoms were refined with anisotropic thermal parameters. The data were corrected for absorption [7]: $T_{\min} = 0.789$ and $T_{\max} = 0.967$.

3. Results and discussion

Diffraction measurements for powdered samples of K_2ReI_6 were performed by Morrow [10]. They indicated an orthorombic unit cell with a = 11.07(5) Å, b = 13.48(7) Å and c = 10.19(5) Å, with four molecules in the unit cell. $(NH_4)_2ReI_6$ crystallizes in the tetragonal space group *P*4/*mnc* (No. 128), $a = b$ = 7.7436(6), c = 11.6403(14) Å, $Z = 2$, D_x = 4.68 g/cm^3, T = 100(1) K. The molecular structure and crystal packing of $(NH)_2ReI_6$ are shown in Figs. 1 and 2.

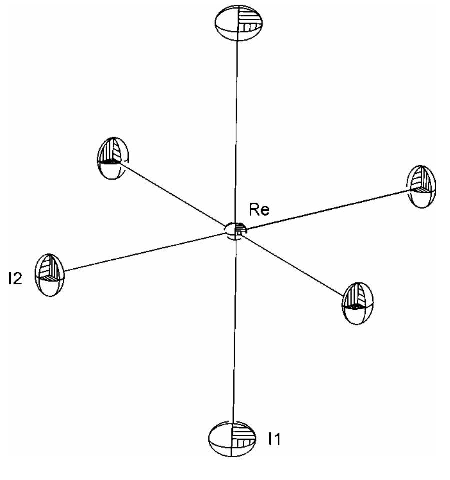

Fig. 1. The molecular structure of $(NH_4)_2ReI_6$

The atomic coordinates and equivalent displacement parameters are given in Table 2. The Re–I1 and Re–I2 bonds are 2.745(4) and 2.715(2) Å, respectively. The bond of 2.745(4) Å is longer and this fact is connected with a special position of the rhenium atoms. The bond lengths Re–I, found from the EXAFS study, were equal to 2.73 Å [11]. The Re–Re distances found in K_2ReCl_6 and K_2ReBr_6 are equal to 6.97 Å and 7.38 Å, the Re–X distances are 2.37 Å and 2.50 Å, and the shortest X–X contacts are 3.62 Å and 3.84 Å [12, 13]. In $(NH_4)_2ReI_6$ the shortest Re–Re distance is 7.74 Å, the Re–I equals 2.73 Å and the shortest contact between I–I in the crystal lattice equals 4.18 Å [Re–I1–I2 ($-0.5 + x$, $-0.5 - y$, $-0.5 + z$)].

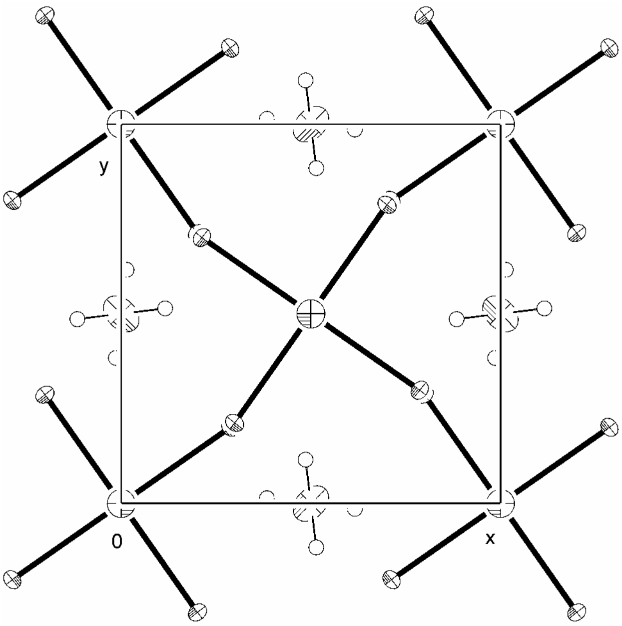

Fig. 2. The crystal packing of $(NH_4)_2ReI_6$ viewed along the [001] direction. The thermal ellipsoids are drawn at 30% probability

Magnetic properties of a series of iodocomplexes have been previously described in literature [14, 15], but the crystal structures were not reported. The effective magnetic moment (μ_{eff}) of $(NH_4)_2ReI_6$ in the solid state is 3.00 B.M. at room temperature, which is consistent with a d^3 electronic configuration in an octahedral geometry. The effective moment 3.00 B.M. is reduced in comparison with the spin-only value (3.87) which can be due to a zero-field splitting and intermolecular interactions. The superexchange mechanism involves an interaction of electrons with opposite spins via intervening diamagnetic anions. This type of interaction has been frequently used to explain the antiferromagnetism of simple oxides and fluorides where metal ions are coupled by a single O^{2-} or F^- ion [16, 17]. In $(NH_4)_2ReI_6$, the rhenium centres are coupled by the I^- ions, and in other hexachalogenorhenates by Cl^- or Br^- ions.

Table 2. Fractional atomic coordinates, equivalent isotropic displacement parameters U_{eq} (in Å^2) with their e.s.d.'s (in parentheses) for $(NH_4)_2ReI_6$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	x	y	z	$U_{\mathrm{eq}}/U_{\mathrm{iso}}$
Re	0	0	0.5	0.0067(6)
I1	0	0	0.2642(3)	0.0289(9)
I2	0.2010(3)	–0.2872(3)	0.5	0.0195(6)
N	0	–0.5	0.25	0.042(14)
H	0.01(4)	–0.383(13)	0.28(2)	0.02(7)

This superexchange path, e.g. with two intervening I^- ions, takes the following form

$$\mathrm{Re} - \mathrm{I} \cdots \mathrm{I} - \mathrm{Re}$$

The magnetic susceptibility (χ_m) was measured from 4 to 300 K and indicated one strong maximum ($T_{\mathrm{Néel}}$) at 20 K. Below 8 K, the magnetic susceptibility data suggest existence of another phase.

The magnetic properties are shown in Fig. 3 in the form of χ_m vs. T and μ_{eff} vs. T. From 10 to 20 K (20 K, $T_{\mathrm{Néel}}$) we observe antiferromagnetic interactions, then paramagnetic ones, but the most interesting are susceptibilities from 10 K to 4 K.

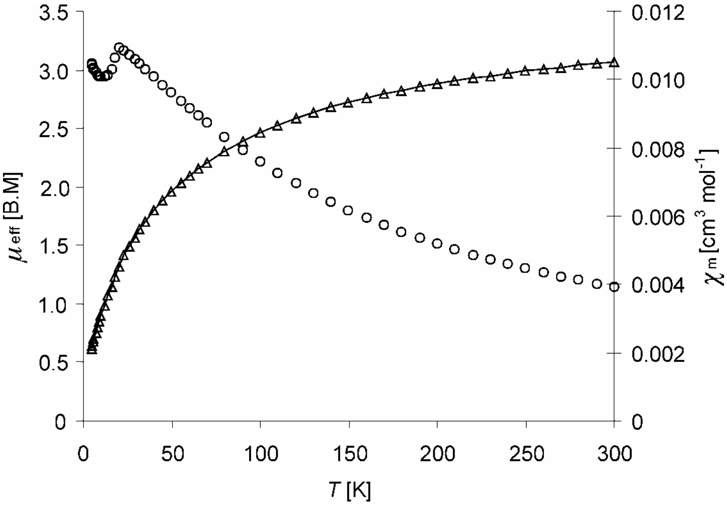

Fig. 3. Plots of χ_m vs. T (o) and μ_{eff} vs. T (Δ) for $(NH_4)_2ReI_6$. The solid line represents the best fit to the experimental data

In this region, the susceptibility runs into another maximum which suggests another phase of ferromagnetic interactions. Unfortunately, an answer will not be possible until a neutron diffraction study or X-ray measurements at the temperature of liquid He is performed. The presence of $T_{\mathrm{Néel}}$ and a strong decrease of the magnetic moment below 200 K and an accompanying change of χ_m suggest the presence of an antiferromagnetic coupling between the rhenium(IV) centres, clearly bridged by the I^- ions. The magnetic susceptibility data are analyzed using the classical spin Hamiltonian [18]:

$$H = 2D\left[S_Z^2 - \frac{1}{3}S(S+1) + g_{\parallel}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) \right] \tag{1}$$

The experimental magnetic data for $(NH)_2ReI_6$ were fitted to the empirical relations proposed earlier [19]

$$\chi_{\parallel}\frac{N\beta^2 g_{\parallel}^2}{4kT}\frac{1+9\exp\left(-\frac{2D}{kT}\right)}{1+\exp\left(-\frac{2D}{kT}\right)}$$

$$\chi_{\perp}=\frac{N\beta^2 g_{\perp}^2}{4kT}\frac{4+6\left(\frac{kT}{2D}\right)\times\left[1+\exp\left(\frac{-2D}{kT}\right)\right]}{1+\exp\left(\frac{-2D}{kT}\right)}$$

where: D is the zero-field splitting, N – Avogadro's number, g – the spectroscopic splitting factor, β – the Bohr magneton, k – the Boltzmann constant and T – the absolute temperature. Since our data concern powdered samples, the experimental magnetic susceptibility χ_{av} equals $(1/3\chi_{\parallel}+2/3\chi_{\perp})$. The best fit parameters were obtained by minimizing the function

$$R=\left[\frac{\sum_{i=1}^{n}\left(\chi_{\mathrm{m}}^{\mathrm{exp}}-\chi_{\mathrm{m}}^{\mathrm{calc}}\right)^2}{\sum_{i=1}^{n}\left(\chi_{\mathrm{m}}^{\mathrm{exp}}\right)^2}\right]^{0.5}$$

The parameters giving the best-fit were obtained using nonlinear regression analysis with $g = 1.93$; $2D = 6.52$ cm^{-1}and $R = 5.12\times10^{-3}$. The magnetic measurements suggest the presence of an antiferromagnetic superexchange interaction at the temperature between 10 and 20 K. At the moment we are unable to explain the temperature dependence of the magnetic susceptibility at low temperatures, from 10 K to 4 K. In $(NH_4)_2ReI_6$ we observed a stronger superexchange than in K_2ReCl_6 and K_2ReBr_6. It is possible that as the electronegativity of the anion decreases, the superexchange increases respectively. Thus, iodide rhenium salts should have stronger superexchange interaction than the chloride and bromide salts.

The antiferromagnetic effect observed is strongly influenced by the crystal structure alone. The symmetry of the ReI_6^{2-} ions and the highly symmetric system into which the compound discussed crystallizes may be connected with a possibility of an antiparalled arrangement of the spins. Rhenium centres, where the central atom itself is already in an octahedral environment, arrange in the cell along particular directions in layers, directly influencing the ordering of the spins located at the Re^{4+} ions. The thermal contraction also positively influences the strength of interactions between the centres which depend strongly on the Re–Re distances. The reduction of volume causes a reduction of the I^-–I^- distances that play a key role in the compound discussed.

Conclusions

The rhenium(IV) salts present antiferromagnetic superexchange interactions between rhenium centres during the I^-–I^- contacts. $T_{\text{Néel}}$ for $(NH_4)_2ReI_6$ is 20 K. These salts can be starting materials for other iodocompounds because the I^- ligands are more labile than Br^- or Cl^- ones. However, their synthesis and crystal growth are very difficult[*].

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Received 7 March 2003
Revised 7 September 2003

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[*] Further details of the investigation of the crystal structure can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax(+49)7247-808-666; e-mail: crysdata@fiz.karlsruhe.de) on quoting depository number CSD-412940.