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The New Inorganic Ligands $TeCl_2$ and $TeBr_2$: Syntheses and Crystal Structures of $Re_6Te_6Cl_6(TeCl_2)_2$ and $[Re_6Te_8(TeBr_2)_6]Br_2$

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Hexanuclear Re_6 chalcogenohalide cluster compounds are well known.[1−6] Most of these are isotypic, having the formula $Re_6Q_{4+q}X_{10-2q}$ (Q = S, Se; X = Cl, Br; $q = 0-4$). The cluster core in this series of compounds is the $Re_6Q_{4+q}X_{4-q}$ unit; it consists of a Re_6 metal−metal-bonded octahedron whose faces are capped with Q and X atoms. The $Re_6Q_4X_{10}$ ($q = 0$) phases are molecular with a terminal X atom bonded to each Re atom,[4,7,8] whereas others exhibit polymeric structures with bridging halogen ligands.[9−13] In the process of developing a high-temperature technique for the synthesis of Te-containing Re_6 cluster compounds, we have prepared two new tellurium-rich Re^{III} compounds: $Re_6Te_6Cl_6(TeCl_2)_2$ (**1**) and $[Re_6Te_8(TeBr_2)_6]Br_2$ (**2**). These contain the new ligands $TeCl_2$ and $TeBr_2$.

Compound **1** was prepared by the reaction of $ReCl_5$ (Strem, 99.9%) with elemental Te (Aldrich, 99.8%) in a 1:2 ratio. Compound **2** was prepared by the reaction of Re_3Br_9 with Te in a 1:2.5 ratio. The syntheses were carried out in evacuated fused silica tubes at 450 °C for 1 d. The tubes were cooled at 4 °C/h to promote crystal growth. The reaction mixtures were washed with CH_3CN, and single crystals were collected. The structures of both compounds (Figure 1 (**1**) and Figure 2 (**2**)) have been determined by single-crystal X-ray diffraction methods.[14]

Compound **1**, $Re_6Te_6Cl_6(TeCl_2)_2$, contains a Re_6 octahedron residing inside a Te_6Cl_2 pseudocube. In the known $Re_6Q_{4+q}X_{10-2q}$ compounds it is usual that each corner of such a cube is occupied statistically by Q and X atoms. However, in the present structure there is no disorder and six of the corners of the Te_6Cl_2 cube are occupied exclusively by Te atoms. The Re−Te distances range from 2.634(3) to 2.711(3) Å; the Re−μ_3-Te distances in Re_6Te_{15}[15] span 2.678(3)−2.709(3) Å. The two other corners of the cube are occupied exclusively by Cl atoms; the Re−μ_3-Cl distances range from 2.476(7) to 2.502(8) Å. The four Re atoms that are bonded to μ_3-Cl ligands have terminal Cl^- ligands. The $Re-Cl_{terminal}$ distances (2.349(9)−2.407(8) Å) are similar to those in the $Re_6Te_4Cl_{10}$ structure (2.325(6)−2.353(5) Å).[6] The two Re atoms that are bonded to μ_3-Te anions are ligated by neutral $TeCl_2$ groups. The Re−$TeCl_2$ distances (2.634(3) to 2.667(3) Å) are comparable to the Re−μ_3-Te distances. The Te−Cl distances in the $TeCl_2$ ligands range from 2.330(9) to 2.363(10) Å.[16] Consistent with this formulation of a neutral $TeCl_2$ ligand containing a Te^{II} atom, the bond angles around Te are approximately tetrahedral. The Cl−Te−Cl bond angles are 88.8(4) and 91.9(4)° and the Re−Te−Cl angles span 105.2(3)−108.4(3)°.

(1) Perrin, A.; Sergent, M. *New J. Chem.* **1988**, *12*, 337−356.
(2) Opalovskii, A. A.; Fedorov, V. E.; Lobkov, E. U.; Erenburg, B. G. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1971**, *16*, 1685.
(3) Yaghi, O. M.; Scott, M. J.; Holm, R. H. *Inorg. Chem.* **1992**, *31*, 4778−4784.
(4) Gabriel, J.-C.; Boubekeur, K.; Batail, P. *Inorg. Chem.* **1993**, *32*, 2894−2900.
(5) Long, J. R.; Williamson, A. S.; Holm, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 226−229.
(6) Mironov, Y. V.; Cody, J. A.; Ibers, J. A. *Acta Crystallogr.* **1996**, *C52*, 281−283.
(7) Leduc, L.; Perrin, A.; Sergent, M.; Le Traon, F.; Pilet, J. C.; Le Traon, A. *Mater. Lett.* **1985**, *3*, 209−215.
(8) Fedorov, V. E.; Mischenko, A. V.; Kolesov, B. A.; Gubin, S. P.; Slovokhotov, Y. L.; Struchkov, Y. T. *Sov. J. Coord. Chem. (Engl. Transl.)* **1985**, *11*, 980−984.
(9) Perrin, A.; Leduc, L.; Sergent, M. *Eur. J. Solid State Inorg. Chem.* **1991**, *28*, 919−931.
(10) Leduc, L.; Padiou, J.; Perrin, A.; Sergent, M. *J. Less-Common Met.* **1983**, *95*, 73−80.
(11) Leduc, L.; Perrin, A.; Sergent, M. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1983**, *39*, 1503−1506.
(12) Fischer, C.; Alonso-Vante, N.; Fiechter, S.; Tributsch, H.; Reck, G.; Schulz, W. *J. Alloys Compd.* **1992**, *178*, 305−314.
(13) Fischer, C.; Fiechter, S.; Tributsch, H.; Reck, G.; Schultz, B. *Ber. Bunsen-Ges. Phys. Chem.* **1992**, *96*, 1652−1658.

(14) Crystal data for $Re_6Te_6Cl_6(TeCl_2)_2$: orthorhombic C_{2v}^9-*Pna*2$_1$, $Z = 4$, $a = 19.099(4)$ Å, $b = 15.211(3)$ Å, $c = 8.902(2)$ Å, $V = 2586.2(9)$ Å^3 at 113 K. $R_w(F^2) = 0.122$ for 217 variables and 6630 independent reflections; $R_1 = 0.062$ for 4409 reflections having $F_o^2 > 2\sigma(F_o^2)$. Crystal data for $[Re_6Te_{14}Br_{12}]Br_2$: trigonal C_{3i}^2-$R\bar{3}$, $Z = 3$, $a = 10.151(2)$ Å, $c = 34.02(1)$ Å, $V = 3036(2)$ Å^3 at 153 K. $R_w(F^2) = 0.204$ for 52 variables and 945 independent reflections; $R_1 = 0.090$ for 683 reflections having $F_o^2 > 2\sigma(F_o^2)$.

(15) Klaiber, F.; Petter, W.; Hulliger, F. *J. Solid State Chem.* **1983**, *46*, 112−120.

(16) The neutral $TeBr_2$ and $TeCl_2$ molecules have been observed as dissociation products of TeX_4 halides[30] and have structures similar to those found here for the coordinated ligands. The Te−X bond distances in these compounds as determined by electron diffraction studies of the gases are 2.329(3) Å for $TeCl_2$[31] and 2.51(2) Å for $TeBr_2$.[32]

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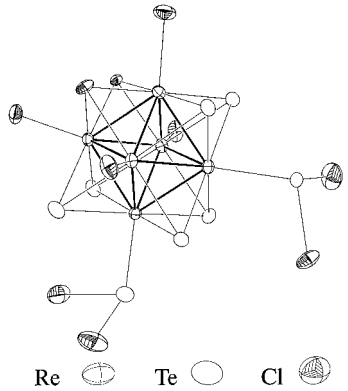

Figure 1. The neutral $Re_6Te_6Cl_6(TeCl_2)_2$ cluster. In this figure and in Figure 2, displacement ellipsoids are drawn at the 75% probability level.

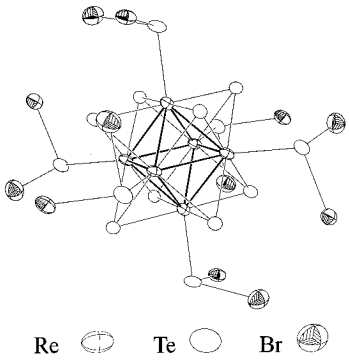

Figure 2. The $[Re_6Te_8(TeBr_2)_6]^{2+}$ cation.

Compound **2**, $[Re_6Te_8(TeBr_2)_6]Br_2$, which has crystallographically imposed $\bar{3}$ symmetry, contains a Re_6 core inscribed in a cube of μ_3-Te ligands; each Re atom in addition is ligated by a neutral $TeBr_2$ group. Re−Re distances (2.666(3)−2.677(4) Å) and Re−μ_3-Te distances (2.638(5)−2.668(3) Å) are comparable to those in the structure of Re_6Te_{15}. In compound **1**, where only two Re atoms are bonded exclusively to μ_3-Te ligands, each cluster contains only two $TeCl_2$ ligands. In compound **2**, all six Re atoms are bonded to μ_3-Te ligands and each Re atom has an attached $TeBr_2$ ligand. The Re−$TeBr_2$ distance is 2.634(3) Å, similar to the Re−$TeCl_2$ distance in compound **1**. The Te−Br bond lengths in the $TeBr_2$ ligands are 2.484(6) and 2.503(6) Å.[16] As in the $TeCl_2$ ligand, the bond angles around the Te atom of the $TeBr_2$ group are nearly tetrahedral. The Br−Te−Br bond angle is 92.0(2)°, and the Re−Te−Br angles are 103.2(2) and 103.6(1)°.

The neutral $TeCl_2$ and $TeBr_2$ ligands described here are new, but related QCl_2 ligands are known. Thus, SCl_2 and $SeCl_2$ ligands are found in the systems $PdCl_2(QCl_2)_2$ (Q = S, Se),[17] $AuCl_3(SCl_2)$,[18] $PtCl_4(SCl_2)_2$, $PdCl_2(SCl_2)_2$,[19] and $Ru_2Cl_5(SCl_2)_4$;[20] some of these compounds have been prepared through the use of the stable SCl_2 molecule. The coordination geometry of these QCl_2 ligands is similar to that found for the QX_2 ligands in the title compounds. For example, Cl−S−Cl bond angles of 97.9(6)−100.2(5)° and Ru−S−Cl bond angles of 109.1(5)−111.9(4)° are found in $Ru_2Cl_5(SCl_2)_4$. Different but related TeX_n-type ligands are also known. Thus the recently prepared $Mo_3Te_{10}I_{10}$ cluster contains the TeI_3^- ligand in which the Te^{II} atom is bonded to two terminal I^- anions and to a third I^- atom that bridges to a Mo center.[21] And compounds containing the TeX_3^+ (X = F, Cl, Br, I) ligand, where Te is in the +IV oxidation state, are also known.[22−29]

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Note Added in Proof. The structure of $Re_4Te_4(TeBr_2)_4Br_8$, which contains the neutral $TeBr_2$ ligand, has just been reported (Schulz Lang, E.; Abram, U.; Strähle, J. *Z. Anorg. Allg. Chem.* **1996**, *622*, 251−253).

Supporting Information Available: Tables of crystallographic details, positional parameters, bond lengths and angles, and anisotropic displacement parameters (14 pages). Ordering information is given on any current masthead page.

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(17) Rybakov, V. B.; Aslanov, L. A.; Vokov, S. V.; Grafov, A. V.; Pekhn'o, V. I.; Fokina, Z. A. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1991**, *36*, 680−682.
(18) Rybakov, V. B.; Aslanov, L. A.; Volkov, S. V.; Fokina, Z. A.; Lapko, V. F. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1991**, *36*, 1423−1425.
(19) Paulus, M.; Thiele, G. *Z. Anorg. Allg. Chem.* **1990**, *588*, 69−76.
(20) Paulus, M.; Thiele, G. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1992**, *47*, 253−257.
(21) Fedin, V. P.; Imoto, H.; Saito, T. *J. Chem. Soc., Chem. Commun.* **1995**, 1559−1560.
(22) Beck, J. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1991**, *46*, 183−186.
(23) Passmore, J.; Sutherland, G.; White, P. S. *Can. J. Chem.* **1981**, *59*, 2876−2878.
(24) Christian, B. H.; Collins, M. J.; Gillespie, R. J.; Sawyer, J. F. *Inorg. Chem.* **1986**, *25*, 777−788.
(25) Jones, P. G.; Jentsch, D.; Schwarzmann, E. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1986**, *41*, 1483−1484.
(26) Passmore, J.; Richardson, E. K.; Whidden, T. K.; White, P. S. *Can. J. Chem.* **1980**, *58*, 851−857.
(27) Beck, J. *Chem. Ber.* **1991**, *124*, 677−681.
(28) Krebs, B.; Buss, B.; Altena, D. *Z. Anorg. Allg. Chem.* **1971**, *386*, 257−269.
(29) Troyanov, S. I.; Rybakov, V. B.; Fokina, Z. A. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1994**, *39*, 356−359.
(30) Krebs, B.; Ahlers, F.-P. *Adv. Inorg. Chem.* **1990**, *35*, 235−317.
(31) Fernholt, L.; Haaland, A.; Volden, H. V.; Kniep, R. *J. Mol. Struct.* **1985**, *128*, 29−31.
(32) Rogers, M. T.; Spurr, R. A. *J. Am. Chem. Soc.* **1947**, *69*, 2102−2103.