Studies of Mixed-valence States in Three-dimensional Halogen-bridged Gold Compounds, $Cs_2Au^IAu^{III}X_6$ (X = Cl, Br or I). Part 1. Synthesis, X-Ray Powder Diffraction, and Electron Spin Resonance Studies of $CsAu_{0.6}Br_{2.6}$‡

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A new non-stoichiometric mixed-valence compound $CsAu_{0.6}Br_{2.6}$ has been prepared, and its powder X-ray diffraction profile, ESR spectra, and electrical conductivity determined. From its empirical formula the average valence of Au is +2.67. Powder diffraction data indicate that the compound has a cubic perovskite structure [cubic lattice, space group *Pm*3*m*, *a* = 5.462(2) Å]. This means that the $AuBr_6$ octahedra are crystallographically equivalent. ESR measurements show the existence of a +II formal oxidation state for Au. The conductivity is four orders of magnitude higher than that of the Au^I–Au^{III} mixed-valence compound $Cs_2Au_2Br_6$.

Caesium gold chloride $Cs_2Au_2Cl_6$ is known as a three-dimensional halogen-bridged mixed-valence system and was first prepared by Wells[1] in 1922. It was described as astonishingly jet black in colour, from which a metal–metal interaction was considered to exist. So this compound was expected to be an Au^I–Au^{III} mixed-valence compound, though the formal oxidation state of gold appeared to be +II from the empirical formula $CsAuCl_3$. The crystal structure was determined by Elliott and Pauling[2,3] in the 1930s. They investigated it by X-ray powder photography and magnetic susceptibility measurements in order to obtain information regarding the valence state of the gold. Four possible structure types were considered which are reminiscent of the Robin–Day mixed-valence concept.[4] Subsequently, much work on $Cs_2Au_2Cl_6$ have been done (*e.g.* high-pressure conductivity,[5] single-crystal X-ray diffraction,[6] high-pressure neutron diffraction,[7] high-pressure single-crystal X-ray diffraction,[8] high-pressure Mössbauer,[9] Mössbauer,[10] X-ray absorption near-edge structure,[11] X-ray photoelectron (XPS),[12] and high-pressure Raman spectroscopy[13]). On the other hand, to our knowledge, there has been little work on $Cs_2Au_2Br_6$ or $Cs_2Au_2I_6$.[14–16]

The purpose of this paper and the succeeding Parts 2[17] and 3[18] is to report a systematic investigation of the mixed-valence states in $Cs_2Au_2X_6$ (X = Cl, Br or I). In Part 1 we will discuss the characteristics of the crystal structure of this mixed-valence system in which linear $[Au^IX_2]^-$ and square-planar $[Au^{III}X_4]^-$ complexes are formed alternately. Consequently, there is an anisotropic three-dimensional $-Au^I-X-Au^{III}-X-$ network which we need to take into consideration in the charge-transfer interaction between the gold(I) and gold(III) ions. Secondly, we will report on a new non-stoichiometric caesium bromoaurate $CsAu_{0.6}Br_{2.6}$. In order to achieve a precise characterization of this compound, we have performed a detailed investigation by X-ray powder diffraction, ESR, electrical conductivity, XPS,[17] and Mössbauer spectroscopy.[18]

Experimental

Preparation of Gold Compounds.—(*a*) $Cs_2Au_2Br_6$. The jet black mixed-valence compound $Cs_2Au_2Br_6$ was prepared by a Bridgeman technique. A powdered mixture of CsBr, Au and $CsAuBr_4$ in the stoichiometric ratio was sealed in an evacuated quartz tube with a capillary. The capsule was placed in a furnace equipped with a temperature gradient of 5 K cm^{-1} (T_{max} about 770 K). The melting point of this compound, as measured by differential scanning calorimetry (DSC), was near 725 K. The cooling rate for growth was *ca.* 0.4 K h^{-1}. The molar ratio of Cs:Au was determined by using a Jarrel Ash AA-8200 atomic absorption and flame emission spectrophotometer at the Research Center of Instrumental Analyses, Kyoto University (Found: Au, 34.1; Cs, 23.6. Calc. for $Au_2Br_6Cs_2$:Au, 34.6; Cs, 23.3%).

(*b*) $CsAu_{0.6}Br_{2.6}$. This new compound was prepared by slow addition of CsBr (0.72 g) dissolved in absolute ethanol (100 cm^3) to $KAuBr_4 \cdot 2H_2O$ (1.50 g) dissolved in absolute ethanol (50 cm^3) and cooling. A jet black product precipitated rapidly and almost quantitatively. It was washed with cold ethanol and dried *in vacuo*. The molar ratio of Cs:Au was determined by the method mentioned above. The molar ratio of Br were determined by energy-dispersive fluorescence X-ray analyses using a Rigaku Ultra-Trace System at the Environment Preservation Center, Kyoto University. The variation in x and y for $CsAu_xBr_y$ between batches prepared in this manner is small ($0.55 < x < 0.65$, $2.5 < y < 2.7$). All measurements recorded in this and the following papers[17,18] were performed for the sample with $x = 0.6$, $y = 2.6$ (Found: Au, 25.7; Br, 44.8; Cs, 28.9. $Au_{0.6}Br_{2.6}Cs$ requires Au, 25.8; Br, 45.2; Cs, 29.0%).

X-Ray Diffraction.—The phase identification of each compound was made with an X-ray diffractometer with monochromatic Cu-Kα radiation. The lattice parameters were determined by least-squares fits to the measured positions of the high-angle reflections.

ESR Spectroscopy.—The ESR measurements were performed on powdered samples using a JEOL X-band spectrometer with a 100 kHz field modulation. Variable temperature from 3.7 to 300 K was provided by means of a flowing-gas cryostat system (Oxford Instruments ESR-900). The temperature of the sample was measured by a AuFe-normal silver thermocouple positioned near the sample. Calibration of g values was based on dpph (diphenylpicrylhydrazyl) (g = 2.0036).

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‡ *Non-SI units employed:* G = 10^{-4} T, eV ≈ 1.60×10^{-19} J.

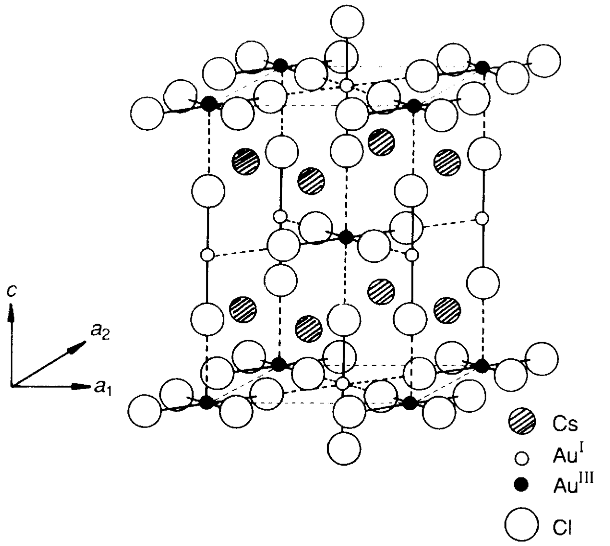

Fig. 1 Crystal structure of $Cs_2Au^IAu^{III}Cl_6$ (space group *I4/mmm*)[3,6]

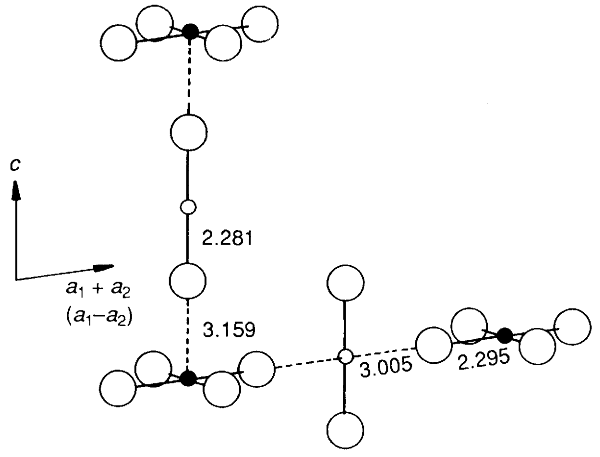

Fig. 2 Anisotropic AuCl chains in $Cs_2Au^IAu^{III}Cl_6$[6]

Electrical Conductivity.—The d.c. electrical conductivity measurements were performed on polycrystalline samples with a quasi-four-probe method. Samples were prepared by pressing powders under pressure of 0.3 GPa into cylindrical pellets, 5 mm in diameter and typically 0.6 mm in thickness.

Results and Discussion

Description of the Structure of $Cs_2Au_2X_6$ (X = Cl, Br *or* I).—The crystal structure of $Cs_2Au_2Cl_6$ is a distorted perovskite with square planar $[Au^{III}Cl_4]^-$ and linear $[Au^ICl_2]^-$ complex ions, with space group *I4/mmm* [tetragonal, a = 7.495(1), c = 10.880(2) Å, Z = 2].[6] As reported by Brauer and Sleater,[15] the powder X-ray diffraction patterns of $Cs_2Au_2Br_6$ and $Cs_2Au_2I_6$ show these two compounds to be isostructural with $Cs_2Au_2Cl_6$. Hence $Cs_2Au_2Br_6$ and $Cs_2Au_2I_6$ have been indexed to *I4/mmm*. Our very recent single-crystal X-ray analysis of $Cs_2Au_2I_6$[19] shows it to belong to the tetragonal space group *I4/mmm*, with a = 8.284(1), c = 12.092(2) Å and Z = 2.

The crystal structure of $Cs_2Au_2Cl_6$ can be characterized by distorted corner-sharing $AuCl_6$ octahedra which form chains in the directions of $a_1 + a_2$, $a_1 - a_2$ and c, where the tetragonal unit cell is (a_1,a_2,c), as shown in Fig. 1. The Au^ICl_6 octahedra are contracted in the c direction, on the other hand the $Au^{III}Cl_6$ ones are elongated in the c direction. The volume of the Au^ICl_6 octahedron (27.46 Å^3) is larger than that of $Au^{III}Cl_6$ (22.18 Å^3). Hence the breathing-mode-type atomic distortion of $AuCl_6$ octahedra is present in this mixed-valence system. This distortion is analogous to that of the mixed-valence bismuth(III,V) oxide $BaBiO_3$ which is the parent compound of the Cu-free high-T_c superconducting oxides $(Ba,K)BiO_3$ and $(Ba,Rb)BiO_3$ ($T_c \approx$ 30 K) and $Ba(Pb,Bi)O_3$ ($T_c \approx$ 13 K).[20–22] By analogy with these three-dimensional superconductors, the following correspondence may occur: $Cs^+ \longleftrightarrow Ba^{2+}$, Au^I, $Au^{III} \longleftrightarrow Bi^{III}$, Bi^V and $X^- \longleftrightarrow O^{2-}$.[23] The insulating state of $BaBiO_3$ was explained as the result of a commensurate charge-density wave (c.c.d.w.) involving the ordering of Bi^{III} and Bi^V into distinct crystallographic sites.[24] Therefore, the structure of $Cs_2Au_2X_6$ might be regarded as frozen in a soft mode of perovskite structure, resulting in a c.c.d.w. and a displacement modulation of the halogen positions. In recent years halogen-bridged one-dimensional M^{II}–M^{IV} mixed-valence complexes of Pt, Pd and Ni analogous to Wolffram's Red Salt have been investigated intensively from the viewpoints of physics and chemistry as a model of one-dimensional systems.[25,26] On the other hand, there has been little work on the three-dimensional halogen-bridged mixed-valence complexes [*e.g.* $Rb_2Au_2X_6$ (X = Br or I),[27] $K_2Au_2I_6$,[28] PtI_3[29] and Pt_3I_8[30]]. Among the three-dimensional halogen-bridged mixed-valence complexes, $Cs_2Au_2X_6$ is a rare system in which the –M–X–M–X– networks are orthogonal to each other. The networks in $Cs_2Au_2Cl_6$ are not isotropic but anisotropic, being $\cdots$ Cl–Au^I–Cl $\cdots$ Au^{III} $\cdots$ in the c direction and $\cdots$ Au^I $\cdots$ Cl–Au^{III}–Cl $\cdots$ in the a_1a_2 plane. In many halogen-bridged one-dimensional mixed-valence complexes of Pt, Pd, Ni and Au the bridging ions lie closer to the more highly oxidized metal cations, as is realized in the a_1a_2 plane of $Cs_2Au_2Cl_6$. It seems strange that the bridging halogens lie closer to the Au^I in the networks in the c direction. Also that the Au^I–Cl distance (2.281 Å) is shorter than Au^{III}–Cl (2.295 Å). In general, as the oxidation state of a metal cation increases, the metal–ligand bond length becomes shorter. This implies that the covalency of the Cl–Au^I–Cl bonds is rather high and that some d–s mixing[31] is present in the valence orbitals in spite of the d^{10} complex ion. If the electron pairs occupying the d_{z^2} orbital of the free ion are put into a $(1/\sqrt{2})$ $(5d_{z^2}$–$6s)$ orbital, the ligand anion can approach more closely to the Au ion due to the promotion of electron density from the d_{z^2} to the s orbital which causes a significant reduction in the magnitude of the repulsion between the metal d_{z^2} and the ligand p_z orbitals. The d–s mixing is important for the analyses of the ^{197}Au Mössbauer spectra and we will discuss it in Part 3.[18]

Fig. 2 shows part of the three-dimensional network in $Cs_2Au_2Cl_6$. From a structural point of view, we consider that the charge-transfer interaction between Au^I and Au^{III} through the bridging halogens would be stronger in the networks in the a_1a_2 plane than those in the c direction, for the following reasons.

(1) The $Au^I \cdots Au^{III}$ distance (5.300 Å) in the networks in the a_1a_2 plane is shorter than that (5.440 Å) in the networks in the c direction.

(2) The ratio $p = |d_1 - d_2|/(d_1 + d_2)$, where d_1 and d_2 are the Au^I–X and Au^{III}–X distances, respectively, is an indication of the deviation of the bridging halogen ion from the midpoint between the gold(I) and -(III) sites. As the charge-transfer interaction becomes stronger, the difference in the oxidation states between Au^I and Au^{III} decreases and p decreases. The value of p in the networks of the a_1a_2 plane (0.13:1) is smaller than that in the networks of the c direction (0.16:1).

(3) The $Au^I \cdots Cl$ distance (3.005 Å) in the networks of the a_1a_2 plane is shorter than $Au^{III} \cdots Cl$ (3.159 Å) in the networks of the c direction.

(4) As mentioned above, in many halogen-bridged one-dimensional mixed-valence complexes, the bridging halogen ions lie closer to the more highly oxidized metal cations, as in the networks in the a_1a_2 plane. This shows that the more highly oxidized metal cations possess unoccupied acceptor orbitals. As pointed out by Robin and Day,[32] the d_{z^2} orbital of the $[Au^ICl_2]^-$ ion and the $d_{x^2-y^2}$ orbital of $[Au^{III}Cl_4]^-$ are orthogonal in the networks of the c direction. On the other

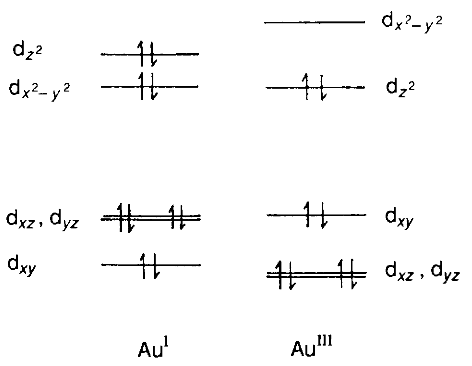

Fig. 3 Schematic energy-level diagram for 5d orbitals of Au^I and Au^{III} in $Cs_2Au_2X_6$

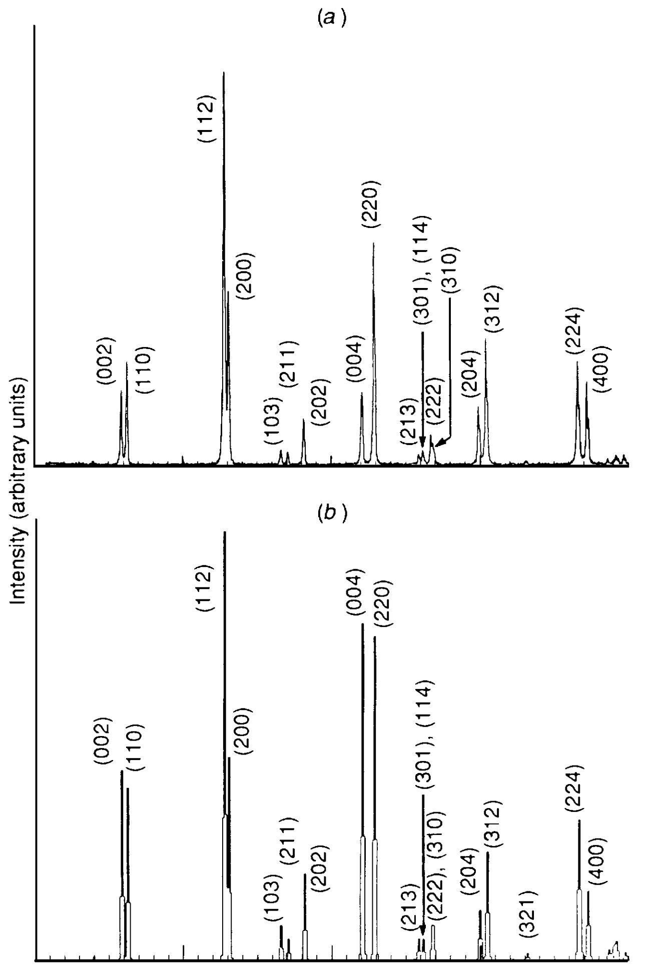

Fig. 4 Powder X-ray diffraction profiles of $Cs_2Au^IAu^{III}Br_6$: (*a*) observed, (*b*) calculated on the space group *I*4/*mmm*. The numbers indicate the indices of the Bragg reflections

hand, those orbitals in the networks of the a_1a_2 plane have non-zero overlap. They considered that the donor and acceptor orbitals were the d_{z^2} orbital of $[Au^ICl_2]^-$ and the $d_{x^2-y^2}$ orbital of $[Au^{III}Cl_4]^-$, respectively. However, the overlap between these orbitals is considered to be small, and both the d_{z^2} orbitals of $[Au^ICl_2]^-$ and $[Au^{III}Cl_4]^-$ are occupied. Therefore, we consider that the charge-transfer interaction in $Cs_2Au_2Cl_6$ is mainly between the donor $d_{x^2-y^2}$ orbital of $[Au^ICl_2]^-$ and the acceptor $d_{x^2-y^2}$ orbital of $[Au^{III}Cl_4]^-$ in the networks of the a_1a_2 plane.

(5) The intervalence charge-transfer absorption spectra have been observed for the halogen-bridged one-dimensional mixed-valence gold complexes $[AuX_2(PhCH_2SCH_2Ph)]$ (X = Cl or Br),[33] which possess networks analogous to those in the a_1a_2 plane of $Cs_2Au_2Cl_6$. Recently, Janiak and Hoffmann[34] have carried out band-structure calculations on $[AuX_2(PhCH_2SCH_2Ph)]$ by using the extended-Hückel method. We have systematically investigated the anisotropic charge-transfer interaction in $Cs_2Au_2X_6$ by changing the bridging halogen X from Cl to I as a method for modifying the interaction, and details on this will be reported in Parts 2 (XPS study)[17] and 3 (Mössbauer study).[18]

Powder X-Ray Diffraction Profiles of Cs–Au–Br *Mixed-valence Compounds.*—The powder X-ray diffraction profile was obtained at room temperature for the $Cs_2Au_2Br_6$ compound prepared by the Bridgeman technique. It is similar to that obtained by other workers[15] for the same compound prepared by thermal decomposition of $CsAuBr_4$. Their work indicated that the compound crystallizes with a structure isomorphous with that of Wells's salt, $Cs_2Au_2Cl_6$, leading to the conclusion that the Br_6 co-ordination octahedra of Au^I and Au^{III} (*i.e.* Au^IBr_6 and $Au^{III}Br_6$) are crystallographically non-equivalent. In the profile obtained, each doublet *e.g.* [(002), (110)], [(112), (200)] is due to the difference between the $Au^I \cdots Au^{III}$ distances in the a_1a_2 plane ($d_{a_1a_2}$ = 5.44 Å) and the *c* direction (d_c = 5.57 Å). The presence of weak superstructure reflections *e.g.* (103), (301) indicates that the Br atoms are shifted from the symmetrical position between the Au atoms. The intensities of the powder lines of $Cs_2Au_2Br_6$ were calculated by assuming a tetragonal space group *I*4/*mmm*, with a = 7.69, c = 11.38 Å, Z = 2, using the atomic scattering factors given by ref. 35 and the positional parameters reported for $Cs_2Au_2Cl_6$.[6] No absorption correction was applied. A typical observed diffraction profile and the calculated profile of the tetragonal phase $Cs_2Au_2Br_6$ are shown in Fig. 4. All the reflections present are indicative of a single phase and do not contradict the distorted perovskite structure with space group *I*4/*mmm*. The agreement between observation and calculation shows that $Cs_2Au_2Br_6$ possesses similar anisotropic MX networks to those of $Cs_2Au_2Cl_6$. The $Cs_2Au_2Br_6$ compound prepared by the Bridgeman technique is, therefore, considered to be a Robin–Day class II[4] mixed-valence compound.

The powder X-ray diffraction profile obtained at room temperature for the compound $CsAu_{0.6}Br_{2.6}$ differs significantly from that of the tetragonal phase. The small number of very sharp peaks indicates the high symmetry of the structure. Weak superstructure reflections were not observed. The intensities of the powder lines were calculated by assuming a cubic lattice, space group *Pm*3*m*, a = 5.46 Å, Z = 1 (the cubic perovskite structure with the Cs atoms on the lattice sites of Sr, the Au atoms on the sites of Ti, and the Br atoms on the sites of O in strontium titanate $SrTiO_3$). The same values of the atomic scattering factors as those in $Cs_2Au_2Br_6$ were used. A typical observed diffraction profile and the calculated profiles of $CsAu_{0.6}Br_{2.6}$ are shown in Fig. 5. In Fig. 5(*b*) each of the Cs, Au and Br sites is fully occupied, while in Fig. 5(*c*) the occupancies of the Cs, Au and Br sites are 1.00, 0.60 and 0.87, respectively. As shown in Fig. 5(*a*) and 5(*c*), the observed diffraction profile can be quantitatively reproduced, taking into account the vacancies of the Au and Br sites. This agreement is consistent with the presence of Au and Br vacancies found by atomic absorption analyses. No weak superstructure reflections in the observed diffraction pattern indicates a simple cubic perovskite structure in which the Au and Br vacancies are distributed randomly in B and X sites of ABX_3, respectively. Therefore any unit cell larger than the ABX_3 perovskite unit cell with a = 5.46 Å can be neglected. From these results, we can conclude that the cubic phase compound $CsAu_{0.6}Br_{2.6}$ is a single phase with a cubic perovskite structure [cubic lattice, space group *Pm*3*m*, a = 5.462(2) Å, Z = 1]. This means that the $AuBr_6$ octahedra are crystallographically equivalent. The compound $Cs_{1.5}(Au^{III}Br_4)(Br_3)_{0.2}Br_{0.3}$, synthesised by Gütlich *et al.*,[16] crystallizes in a

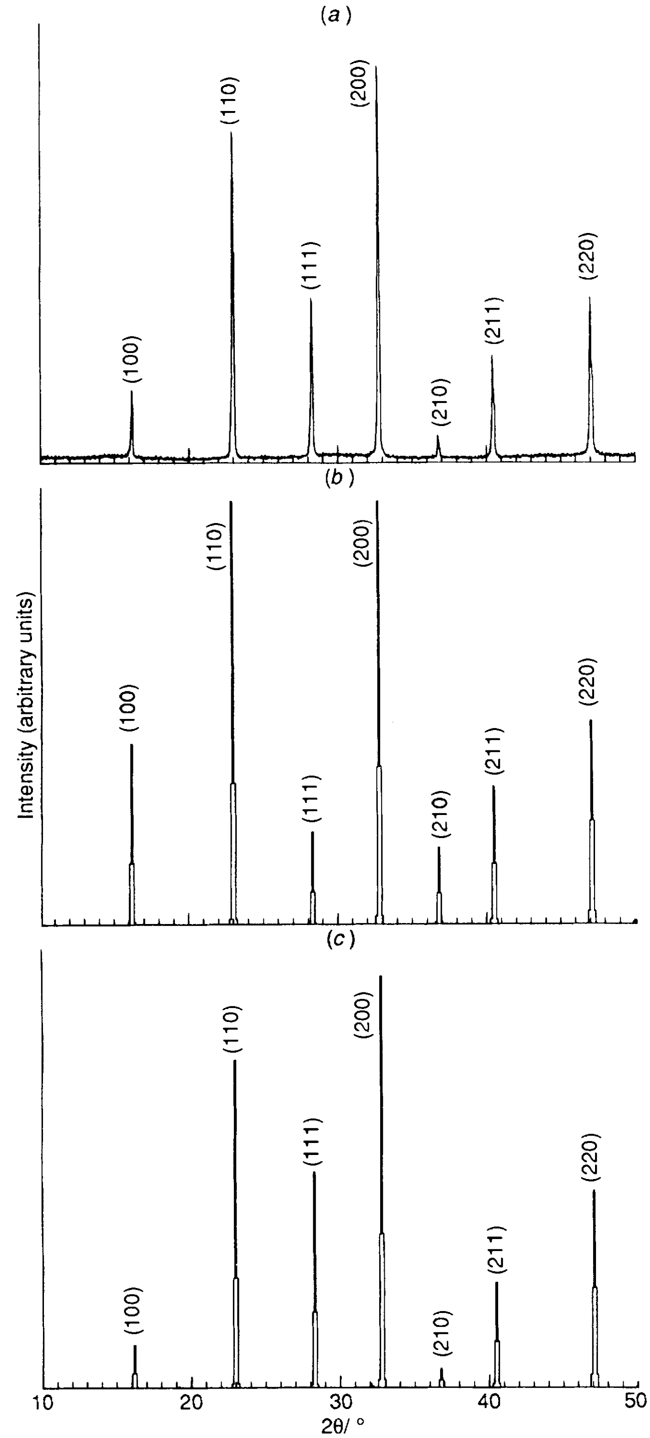

Fig. 5 Powder X-ray diffraction profiles of $CsAu_{0.6}Br_{2.6}$: (*a*) observed, (*b*) calculated on the space group *Pm*3*m* with full occupancies for the Cs, Au, Br sites, and (*c*) calculated based on the space group *Pm*3*m* with occupancies 1.00, 0.60, 0.87 for the Cs, Au, Br sites, respectively

disordered cubic perovskite structure with a = 5.475 Å. However, the compositional ratio and the lattice constant differ from those of $CsAu_{0.6}Br_{2.6}$.

ESR Spectra of the Cubic Phase.—The valence state Au^{II} was hitherto unknown for gold complexes having infinite chains. Therefore, whether the gold ion in the non-stoichiometric compound $CsAu_{0.6}Br_{2.6}$ is present in a +II formal oxidation state or not is of great interest. A gold(II) complex would have one unpaired electron due to the $5d^9$ configuration. Since naturally occurring gold consists of 100% ^{197}Au, which has a nuclear spin of $\frac{3}{2}$, solutions of gold(II) complexes would be expected to give rise to ESR spectra consisting of four equally separated and equally intense lines. A solid complex would also be expected to display paramagnetic behaviour. To investigate the oxidation state of Au in $CsAu_{0.6}Br_{2.6}$ ESR measurements were carried out. In the solid state the spectrum consisted of one broad line. The observed X-band ESR spectra at 3.7, 77 and 290 K are shown in Fig. 6. The observed g value is constant (2.12) in this temperature range and close to the free-spin value (see below). The breadth of the ESR absorption line, ΔH (peak-to-peak width), is temperature independent (315 G).

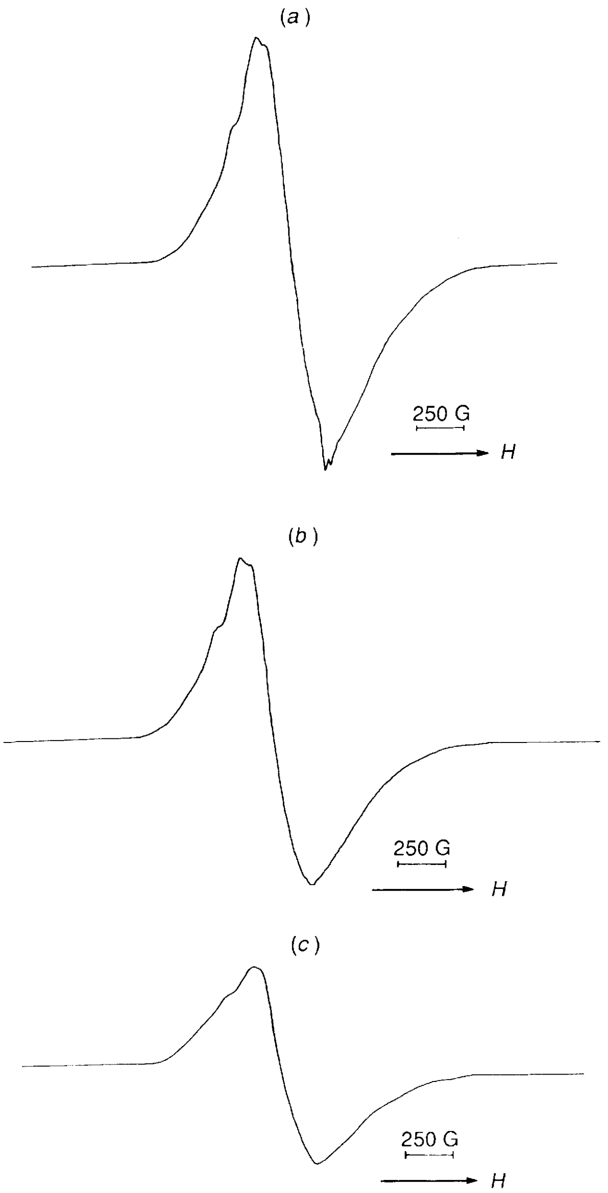

Fig. 6 Powder ESR spectra of $CsAu_{0.6}Br_{2.6}$ observed at (*a*) 3.7, (*b*) 77 and (*c*) 290 K

The compound $CsAu_{0.6}Br_{2.6}$ has a cubic perovskite structure, in which a large part of the gold ions are considered to be in a cubic field (six-fold co-ordination). In such a field the orbital ^2D state ($5d^9$) splits into an orbital doublet $\Gamma_3(^2E_g)$ and an orbital triplet $\Gamma_5(^2T_{2g})$, the former being the lower in energy. In the ground state $\Gamma_3(^2E_g)$ there is no first-order contribution arising from the spin–orbit interaction to the g value. Therefore the observed g value is expected to be close to the free-spin value. The spin–lattice relaxation time τ_1 is also expected to be long. However the breadth of the ESR absorption line is considerably larger than one would expect, and is considered to be caused by the non-stoichiometry, an unresolved hyperfine

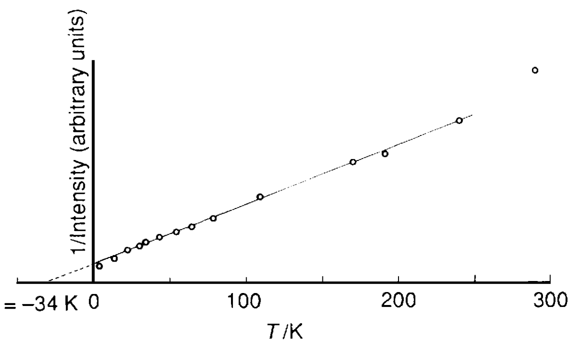

Fig. 7 The reciprocal of the ESR signal intensity of $CsAu_{0.6}Br_{2.6}$ as a function of temperature

structure, and the interaction between the magnetic dipoles. As shown in Fig. 7, the ESR intensity (*i.e.* spin susceptibility) of $CsAu_{0.6}Br_{2.6}$ follows the Curie–Weiss law with $\theta = -34$ K. The large negative Weiss constant implies antiferromagnetic interaction between the gold ions. Despite this, the antiferromagnetic transition does not take place on cooling to 3.7 K, probably due to the dilute random spin system. It should be noted that the critical concentration of a diluted three-dimensional Heisenberg-type antiferromagnet, at the temperature at which the magnetic phase transition becomes zero, is 60%.[36] In the case of $CsAu_{0.6}Br_{2.6}$ the proportion of gold occupancy is 60%.

Electrical Conductivity.—For $CsAu_{0.6}Br_{2.6}$ a thermally activated semiconducting behaviour was observed in the temperature range 300–240 K. The electrical conductivity at room temperature is *ca.* 10^{-4} S cm^{-1}, whereas that of $Cs_2Au_2Br_6$ is *ca.* 10^{-8} S cm^{-1}. The activation energy E_a, where $\sigma = \sigma_0 \exp(-E_a/k_BT)$, is 0.36 eV (between 300 and 240 K) for $CsAu_{0.6}Br_{2.6}$, whereas it is 0.46 eV (between 373 and 270 K) for $Cs_2Au_2Br_6$.

From the powder X-ray diffraction, the gold sites in the crystal structure of $CsAu_{0.6}Br_{2.6}$ are indistinguishable. The ESR spectra and the considerable increase in electrical conductivity due to the partial oxidation were observed for $CsAu_{0.6}Br_{2.6}$. This behaviour is analogous to that of $K_2Pt(CN)_4Br_{0.3}\cdot nH_2O$[37] which is a class III mixed-valence system, according to the Robin–Day classification.[4] Accordingly, it can be concluded that the cubic phase $CsAu_{0.6}Br_{2.6}$ is also a class III mixed-valence system.

Conclusion

From a structural point of view, we have discussed the anisotropy in the three-dimensional MX networks of the mixed-valence system $Cs_2Au_2X_6$. The present study and the results of physical measurements for the cubic phase $CsAu_{0.6}Br_{2.6}$ are consistent with 'class-III mixed-valence compounds' according to the classification of Robin and Day. From the ESR experimental results, the oxidation state Au^{II} is present in $CsAu_{0.6}Br_{2.6}$.

Acknowledgements

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References

1 H. L. Wells, *Am. J. Sci.*, 1922, **3**, 315.
2 N. Elliott, *J. Chem. Phys.*, 1934, **2**, 419.
3 N, Elliott and L. Pauling, *J. Am. Chem. Soc.*, 1938, **60**, 1846.
4 M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 247.
5 R. Keller, J. Fenner and W. B. Holzapfel, *Mater. Res. Bull.*, 1974, **9**, 1363.
6 J. C. M. Tindemans-v. Eijndhovcn and G. C. Verschoor, *Mater. Res. Bull.*, 1974, **9**, 1667.
7 P. Day, C. Vettier and G. Parisot, *Inorg. Chem.*, 1978, **17**, 2319.
8 W. Denner, H. Schulz and H. d'Amour, *Acta Crystallogr., Sect. A*, 1979, **35**, 360.
9 J. Stanek, *J. Chem. Phys.*, 1982, **76**, 2315.
10 M. Katada, Y. Uchida, K. Sato, H. Sano, H. Sakai and Y. Maeda, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 444.
11 H. Tanino and K. Takahashi, *Solid State Commun.*, 1986, **59**, 825.
12 N. Kojima, H. Kitagawa, T. Nakajima, T. Ban and I. Tsujikawa, *Proceedings of the 25th International Conference on Coordination Chemistry*, Nanjing, 1987, A2-197.
13 H. Tanino, K. Syassen, Z. Wang, M. Hanfland and K. Takahashi, *Proceedings of the 12th AIRAPT and 27th EHPRG International Conference on High Pressure Science and Technology, Paderborn*, 1989.
14 A. Ferrari and M. E. Tani, *Gazz. Chim. Ital.*, 1959, **89**, 502.
15 G. Brauer and G. Sleater, *J. Less-Common Met.*, 1970, **21**, 283.
16 P. Gütlich, B. Lehnis, K. Römhild and J. Strähle, *Z. Naturforsch., Teil B*, 1982, **37**, 550.
17 H. Kitagawa, N. Kojima and T. Nakajima, following paper.
18 H. Kitagawa, N. Kojima and H. Sakai, *J. Chem. Soc., Dalton Trans.*, in the press.
19 N. Matsushita, H. Kitagawa and N. Kojima, unpublished work.
20 A. W. Sleight, J. L. Gillson and P. E. Bierstedt, *Solid State Commun.*, 1975, **17**, 27.
21 L. F. Mattheiss, E. M. Georgy and D. W. Johnson, jun., *Phys. Rev. B*, 1988, **37**, 3745.
22 R. J. Cava, B. Batlogg, J. J. Krajewski, R. C. Farrow, L. W. Rupp, jun., A. E. White, K. T. Short, W. F. Pevk, jun. and T. Y. Kometani, *Nature (London)*, 1988, **332**, 814.
23 I. Tsujikawa, *Jpn. J. Appl. Phys., Ser. 1*, 1988, 155; N. Kojima, H. Kitagawa, T. Ban, F. Amita and M. Nakahara, *Solid State Commun.*, 1990, **73**, 743.
24 D. E. Cox and A. W. Sleight, *Solid State Commun.*, 1976, **19**, 969.
25 H. J. Keller, in *Extended Linear-chain Compounds*, ed. J. S. Miller, Plenum, New York, 1982, vol. 1, p. 357.
26 K. Nasu, *J. Phys. Soc. Jpn.*, 1983, **52**, 3865; 1984, **53**, 302, 427.
27 J. Strähle, J. Gelinek and M. Kölmel, *Z. Anorg. Allg. Chem.*, 1979, **456**, 241.
28 J. Strähle, J. Gelinek, M. Kölmel and A.-M. Nemecek, *Z. Naturforsch., Teil B*, 1979, **34**, 1047.
29 G. Thiele, M. Steiert, D. Wagner and H. Wochner, *Z. Anorg. Allg. Chem.*, 1984, **516**, 207.
30 G. Thiele, W. Weigl and H. Wochner, *Z. Anorg. Allg. Chem.*, 1986, **539**, 1986.
31 L. E. Orgel, *J. Am. Chem. Soc.*, 1958, **80**, 4186.
32 M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 363.
33 H. Tanino, K. Takahashi, M. Tajima, M. Kato and T. Yao, *Phys. Rev. B*, 1989, **38**, 8327.
34 C. Janiak and R. Hoffmann, *Inorg. Chem.*, 1989, **28**, 2743.
35 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
36 T. Oguchi and T. Obokata, *J. Phys. Soc. Jpn.*, 1969, **27**, 1111.
37 *Extended Linear-chain Compounds*, ed. J. S. Miller, Plenum, New York, 1982, vols. 1 and 2.

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