Synthesis and Crystal Structure of $AgTl_3(Cr_2O_7)_2$

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Red single crystals of $AgTl_3(Cr_2O_7)_2$ were prepared *via* high oxygen pressure synthesis as well as by hydrothermal autoclave techniques. Initially, $AgTl_3(Cr_2O_7)_2$ was obtained from a reaction of stoichiometric mixtures of Ag_2O, Cr and $TlNO_3$ under elevated oxygen pressures. Following an optimized approach, the title compound can be synthesized at mild hydrothermal conditions, starting from $AgNO_3$, $TlNO_3$ and $K_2Cr_2O_7$ in aqueous solution. $AgTl_3(Cr_2O_7)_2$ crystallizes in space group $C2/c$ (no. 15) with a = 10.3638(3), b = 10.4817(3), c = 13.4717(4) Å, β = 106.55(1)°, V = 1402.80(5) Å^3, and Z = 4. The structure refinement was based on 3554 independent reflections and resulted in $R1$ = 2.13 %, $wR2$ = 4.54 %. The crystal structure contains independent $Cr_2O_7{}^{2-}$ anions, which are surrounded by silver and thallium cations forming layers that are stacked perpendicular to the *bc* plane.

Key words: Silver, Thallium, Hydrothermal Synthesis, Crystal Structure

Introduction

As a general feature, compounds which comprise closed shell d^{10} species, *e. g.* Ag^I, tend to develop cluster-like aggregates of the d^{10} cations, adopting geometries and partial structures that correspond closely to those found in the bulk metals [1]. For silver-rich ternary oxides such homoatomic d^{10}-d^{10} interactions are often associated with specific physical properties, for instance with respect to spectroscopic behavior or to electronic conductivity [1 – 5]. Also among cations bearing lone pairs, a similar kind of non-classical bonding has been discussed, with the pertinent effects being featured most strikingly by Tl^+ [6, 7]. In order to check if these different kinds of homonuclear interactions influence each other, we have started to combine Ag^+ and Tl^+ as countercations in solids containing complex oxoanions. The first example now encountered does not show any short M^+–M^+ distances, the presence of non-classical bonding effects thus being excluded.

Experimental Section

Synthesis

Single crystals of $AgTl_3(Cr_2O_7)_2$ were initially prepared by reacting Ag_2O (freshly precipitated), $TlNO_3$ (Sigma-Aldrich, 98 %) and elemental chromium (Fluka, 99 %) in stainless-steel autoclaves at elevated oxygen pressures. Equimolar amounts of the starting materials were finely ground in an agate mortar and placed into gold tubes, which were sealed from one side and crimped (not gas tight) from the other. As a mineralizer 1 mL of 3M KOH was added to the starting mixture. Red crystals of $AgTl_3(Cr_2O_7)_2$ were obtained under an oxygen pressure of 34 MPa upon annealing within the temperature range of 350 to 400 °C for 5 d. The yield of $AgTl_3(Cr_2O_7)_2$ was poor, with the main part of the recovered material consisting of non-reacted Ag_2O and Tl_2O_3. Pure bulk material has become accessible along an optimized preparation route under hydrothermal conditions. The reagent-grade chemicals $AgNO_3$, $TlNO_3$ and $K_2Cr_2O_7$ were used as starting materials. In a typical experiment, 170 mg $AgNO_3$ (1 mmol), 798 mg $TlNO_3$ (3 mmol), 588 mg $K_2Cr_2O_7$ (2 mmol) and 15 mL deionized water were combined and reacted for 10 d at 200 °C in a Teflon-lined steel autoclave (inner volume: 30 mL). The crystalline product was filtered off after the reaction, washed with water and dried in air. $AgTl_3(Cr_2O_7)_2$ was obtained in form of red needles and is stable towards air and water. Its composition and phase purity were confirmed by X-ray powder diffraction and EDX (Philips ESEM XL 30 equipped with an EDAX detector) analysis (Ag/Tl/Cr ratio in $AgTl_3(Cr_2O_7)_2$ = 1.07 : 2.99 : 4.01).

X-Ray investigations

X-Ray investigations on powder samples were performed using high-resolution powder diffraction data (D8, Bruker,

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Table 1. Crystallographic data and structure refinement for $AgTl_3(Cr_2O_7)_2$.

Formula	$AgTl_3(Cr_2O_7)_2$
M_r	1152.98
Crystal size, mm^3	0.060 × 0.035 × 0.030
Crystal system	monoclinic
Space group	$C2/c$
a, Å	10.3638(2)
b, Å	10.4817(2)
c, Å	13.4717(3)
β, deg	106.55(1)
V, $Å^3$	1402.80(5)
Z	4
D_{calcd}, g cm^{-3}	5.46
$\mu(MoK_\alpha)$, cm^{-1}	38.7
$F(000)$, e	1992
hkl range	±17, ±17, ±22
Refl. measured / unique / R_{int}	17827 / 3554 / 0.033
Param. refined	102
$R(F) / wR(F^2)^a$ (all refl.)	0.0213 / 0.0454
GoF $(F^2)^b$	1.097
$\Delta\rho_{fin}$ (max/min), e $Å^{-3}$	2.02 / −1.54

[a] $R1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$, $w = [\sigma^2(F_o{}^2)+(AP)^2+BP]^{-1}$, where $P = (\mathrm{Max}(F_o{}^2, 0)+2F_c{}^2)/3$ and A and B are constants adjusted by the program; [b] GoF $= S = [\Sigma w(F_o{}^2 - F_c{}^2)^2/(n_{obs} - n_{param})]^{1/2}$, where n_{obs} is the number of data and n_{param} the number of refined parameters.

Table 2. Atomic positions and equivalent isotropic displacement parameters U_{eq} [a] for $AgTl_3(Cr_2O_7)_2$.

Atom	W.-position	x/a	y/b	z/c	U_{eq} / $Å^2$
Ag(1)	4*e*	1/2	−0.0534(1)	1/4	0.0233(1)
Tl(1)	8*f*	0.5643(1)	0.1827(1)	0.5013(1)	0.0242(1)
Tl(2)	4*e*	1/2	−0.4742(1)	1/4	0.0278(1)
Cr(1)	8*f*	0.2013(1)	0.0711(1)	0.5452(1)	0.0125(1)
Cr(2)	8*f*	0.2913(1)	0.2398(1)	0.2562(1)	0.0143(1)
O(1)	8*f*	0.1412(2)	0.1541(3)	0.6391(2)	0.0239(5)
O(2)	8*f*	0.3660(2)	0.0638(3)	0.5800(2)	0.0253(5)
O(3)	8*f*	0.1472(3)	0.1447(3)	0.4368(2)	0.0306(5)
O(4)	8*f*	0.1415(3)	−0.0712(2)	0.5342(3)	0.0355(6)
O(5)	8*f*	0.1280(2)	0.2537(2)	0.2190(2)	0.0208(4)
O(6)	8*f*	0.3363(3)	0.0949(3)	0.2909(2)	0.0340(6)
O(7)	8*f*	0.3487(3)	0.2846(3)	0.1621(2)	0.0310(6)

[a] $U_{eq} = \frac{1}{3}[U_{22} + 1/\sin^2\beta(U_{11} + U_{33} + 2U_{13}\cos\beta)]$.

$CuK_{\alpha1}$ radiation from a primary Ge(111) Johannson-type monochromator, recorded at r. t.) collected in the range of 5 to 90 degrees in 2θ. The single-crystal diffraction data were collected on a Bruker AXS Smart-CCD diffractometer (MoK_α radiation, graphite monochromator). A data reduction, including corrections for Lorentz and polarization effects as well as absorption effects, was carried out [8, 9]. The structure was solved using the program package SHELXS-97 [10] with Direct Methods and refined by using full-matrix least-squares techniques in SHELXL-97 [10]. All atoms were refined with anisotropic displacement parameters. For technical details of data acquisition and selected crystallographic data, see Tables 1 – 3.

Table 3. Selected interatomic distances (Å) and angles (deg) for $AgTl_3(Cr_2O_7)_2$. Estimated standard deviations are given in parentheses.

Ag(1)–O(2)	2.318(2) [2 ×]	O(2)–Cr(1)–O(1)	111.4(1)
Ag(1)–O(5)	2.517(2) [2 ×]	O(3)–Cr(1)–O(1)	108.0(1)
Ag(1)–O(6)	2.476(3) [2 ×]	O(3)–Cr(1)–O(2)	110.4(1)
Cr(1)–O(1)	1.787(2)	O(3)–Cr(1)–O(4)	109.7(2)
Cr(1)–O(2)	1.639(2)	O(4)–Cr(1)–O(1)	108.4(2)
Cr(1)–O(3)	1.604(2)	O(4)–Cr(1)–O(2)	109.0(2)
Cr(1)–O(4)	1.605(3)	O(5)–Cr(2)–O(1)	109.1(1)
Cr(2)–O(1)	1.776(2)	O(6)–Cr(2)–O(1)	110.0(1)
Cr(2)–O(5)	1.629(2)	O(6)–Cr(2)–O(5)	111.1(2)
Cr(2)–O(6)	1.619(3)	O(7)–Cr(2)–O(1)	107.0(1)
Cr(2)–O(7)	1.615(2)	O(7)–Cr(2)–O(5)	108.4(1)
Tl(1)–O(1)	2.957(1)	O(7)–Cr(2)–O(6)	111.1(2)
Tl(1)–O(2)	2.854(1)	Cr(2)–O(1)–Cr(1)	136.9(1)
Tl(1)–O(2)	2.975(2)	O(2)–Ag(1)–O(2)	174.6(1)
Tl(1)–O(3)	3.133(2)	O(2)–Ag(1)–O(5)	89.7(1)
Tl(1)–O(4)	2.700(3)	O(2)–Ag(1)–O(5)	86.0(1)
Tl(1)–O(5)	2.895(1)	O(2)–Ag(1)–O(6)	93.7(1)
Tl(1)–O(7)	2.816(1)	O(2)–Ag(1)–O(6)	89.7(1)
Tl(1)–O(7)	3.140(1)	O(5)–Ag(1)–O(5)	73.2(2)
Tl(2)–O(1)	3.030(1) [2 ×]	O(6)–Ag(1)–O(5)	165.5(1)
Tl(2)–O(3)	2.833(1) [2 ×]	O(6)–Ag(1)–O(5)	92.3(1)
Tl(2)–O(5)	2.821(1) [2 ×]	O(6)–Ag(1)–O(6)	102.2(2)
Tl(2)–O(7)	3.033(1) [2 ×]		

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-421926.

Results and Discussion

$AgTl_3(Cr_2O_7)_2$ is best prepared under hydrothermal conditions in Teflon-lined steel autoclaves. After a reaction time of 10 d red needles can be harvested in large amounts. The phase purity was confirmed by XRD powder diffraction. The experimental X-ray powder diffraction pattern has been indexed monoclinically, with the refined lattice parameters a = 10.3638(2), b = 10.4817(2), c = 13.4717(3) Å and β = 106.55(4)°. The structure of $AgTl_3(Cr_2O_7)_2$ is not isostructural with any of the known silver or thallium dichromates (*e. g.* $Ag_2Cr_2O_7$ or $Tl_2Cr_2O_7$) [11 – 13]. $AgTl_3(Cr_2O_7)_2$ is the first chromate(VI) containing both Ag and Tl in the cationic part of the crystal structure. The refinement of the occupation factors of Ag and Tl did not indicate any mutual substitution of these atoms on the respective different crystallographic sites. The crystal structure exhibits common coordination polyhedra for all atoms involved (Fig. 1). The X-ray

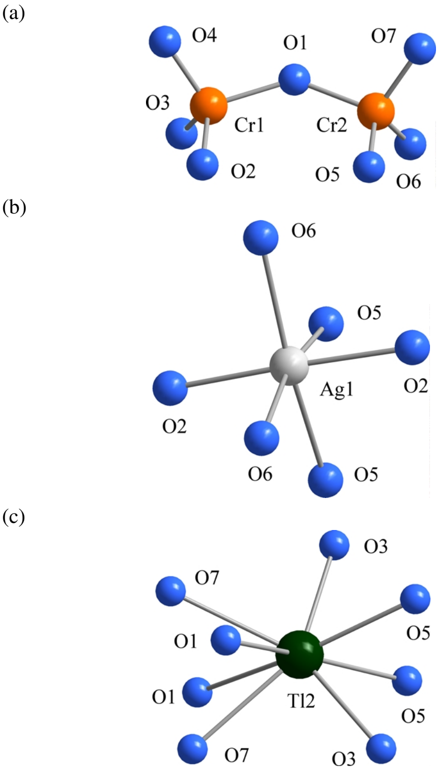

Fig. 1. Coordination environments of Ag, Tl and Cr in $AgTl_3(Cr_2O_7)_2$.

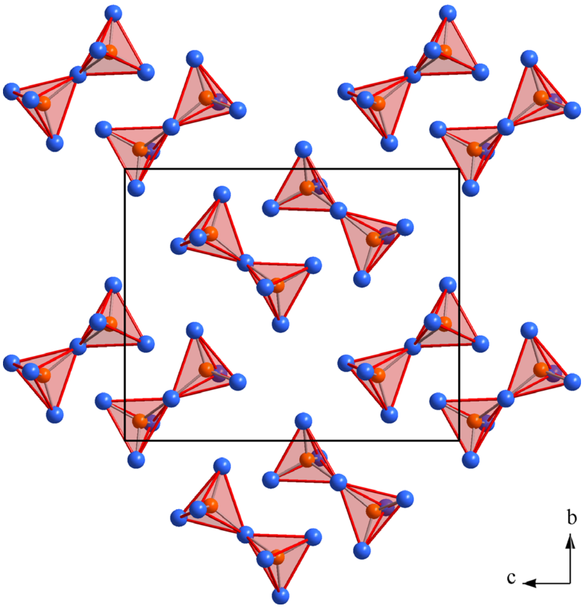

Fig. 2. Arrangement of the $Cr_2O_7{}^{2-}$ anions within the *bc* plane.

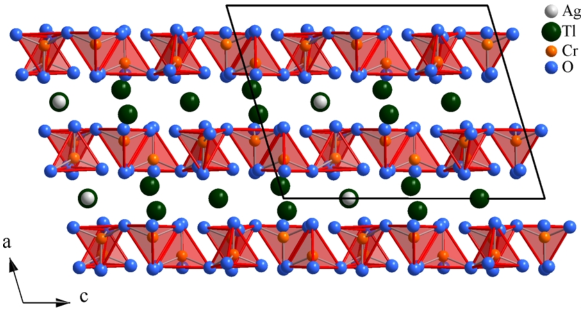

Fig. 3. View of the crystal structure of $AgTl_3(Cr_2O_7)_2$ along [010].

single-crystal structure determination has established that the coordination sphere of Ag consists of six oxygen atoms. The resulting distorted AgO_6 octahedron has typical geometric parameters with Ag–O distances varying from 2.318 to 2.518 Å and angles between 73.2 and 174.6° [1–5]. The thallium cations (Tl1 and Tl2) are in contact with eight oxygen atoms at distances ranging from 2.700 to 3.140 Å, forming TlO_8 square antiprisms. Finally, the $Cr_2O_7{}^{2-}$ dianion, consisting of two crystallographically independent CrO_4 tetrahedra sharing one oxygen atom (atom O1), is featuring a pseudo *syn*-C_{2v} conformation with eclipsed oxygen atoms. This conformation is the usual one for dichromates, and the geometry is fairly regular with a Cr–O–Cr bridging angle of 137°. The Cr–O bridging distances (d = 1.776–1.787 Å) are, as expected, longer than the terminal Cr–O bonds with an average of 1.619 Å. This is in good agreement with typical values found for chromates(VI) and dichromates(VI) [11–14]. The individual $Cr_2O_7{}^{2-}$ units are arranged in pairs within the *bc* plane, with neighbouring pairs rotated by 90°, thus generating an approximate tetragonal tiling (Fig. 2). These dichromate layers are embedded by silver and thallium cations, with a layered structure stacked perpendicular to the *bc* plane (Fig. 3). The silver and thallium ions tend to separate (Fig. 3), however, and no short Ag^+-Ag^+, Tl^+-Tl^+ or Ag^+-Tl^+ contacts can be identified. The shortest Ag–Tl distance amounts to 3.845 Å, which is close to the sum of the respective van der Waals radii (3.68 Å) [15].

Conclusion

Both silver(I) and thallium(I), respectively, have previously been shown to develop unconventional *homo*atomic weak bonding interactions in cation rich compounds. For the purpose of monitoring similar *hetero*atomic interactions we have started to investigate mixed silver(I) and thallium(I) chromates. The title compound $AgTl_3(Cr_2O_7)_2$, however, shows neither *homo*atomic nor *hetero*atomic interactions of that kind.

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