

ihn keine Fehlergrenze explizite angeben lässt. Die Struktur von  $\text{Pb}_2\text{SiO}_4$  bzw.  $\text{Pb}_2(\text{Si,Ge})\text{O}_4$  kann somit durch die zuletzt aufgeführten Gruppoidfamilie sinnvoll charakterisiert werden.

Zur Bestimmung der Gitterkonstanten diente das Programm *RSLC-3* des *UNICS*-Systems (Sakurai, 1967); die Abstände und Winkel wurden mit Hilfe des Programms *ORFFE* (Busing, Martin & Levy, 1964) berechnet. Herrn K. Hirota MSc (Mukizaishitsu Kenkyusho) bin ich für die Überlassung der von ihm gezüchteten Kristalle sowie für die Durchführung der Analysen zum aufrichtigen Dank verpflichtet.

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## Tripotassium *cis*-Dichloro(hydrogendisulfito)platinate(II), $\text{K}_3[\text{Pt}\{(\text{SO}_3)_2\text{H}\}\text{Cl}_2]$ . A Case of an Extremely Short Hydrogen Bond $\text{O}\cdots\text{H}\cdots\text{O}$

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#### Abstract

$\text{K}_3[\text{Pt}\{(\text{SO}_3)_2\text{H}\}\text{Cl}_2]$  crystallizes in the orthorhombic space group  $Cmc2_1$ , with  $a = 15.134$  (3),  $b = 10.490$  (3),  $c = 7.054$  (1) Å,  $Z = 4$ . The structure has been determined by Patterson and Fourier methods and refined to unweighted and weighted  $R$  values of  $R = 0.0206$  and  $R_w = 0.0254$  for 1606 unique reflexions. In the complex anion with mirror symmetry the nearly planar surroundings of the Pt atom are built up by two Cl and two S-coordinated sulfite ligands in the *cis* position. Rather short Pt–S and unusually long Pt–Cl distances [2.247 (2) and 2.388 (2) Å, respectively] indicate a strong *trans* influence of the sulfite ligand. These sulfite ligands are linked by a remarkably short intramolecular hydrogen bond [O $\cdots$ H $\cdots$ O distance 2.382 (6) Å] leading to ring closure. This nearly linear hydrogen bridge is probably symmetric; however, a statistical distribution of the proton in a symmetric double-minimum potential may also be possible. The

anions are connected by one kind of K ion (trigonal prismatic coordination by four Cl and two O atoms from three different anions) to form layers which in turn are linked by a second kind of K ion with highly irregular surroundings.

#### Introduction

In the course of our investigations of heavy-metal compounds containing metal to chalcogen bonds we have laid some emphasis on sulfite complexes of the platinum metals, and mainly of platinum itself (Bauer, 1979). Reviewing the relevant papers in the field, we found some inconsistent and even contradictory results. For instance, crystalline reaction products obtained from potassium sulfite–tetrachloroplatinate(II) systems under identical conditions have been described as  $\text{K}_3[\text{Pt}(\text{SO}_3\text{H})(\text{SO}_3)\text{Cl}_2]$  (Lebedinskii & Novozhenyuk,

1951) or as  $K_2[Pt(SO_3)_2] \cdot 2H_2O$  (Newman & Powell, 1963). Our reinvestigations of these reactions yielded a compound with an IR spectrum identical with that given for  $K_2[Pt(SO_3)_2] \cdot 2H_2O$  by Newman & Powell (1963) but with a composition as determined by the Russian group. In order to reveal the real nature of this compound an X-ray structure analysis has been performed.

### Experimental

9.7 g (20 mmol)  $K_2PtCl_6$  and 1.4 g (10 mmol)  $K_2CO_3$  were dissolved in 10 ml of water, in the presence of  $SO_2$  and with slight heating. The reaction was stopped after dissolution and decolorization; precipitation of the compound was achieved by addition of acetone (*ca* 50 ml). Satisfactory analytical data have been obtained [calc. (%): H 0.19; Cl 13.02; K 21.55; Pt 35.83;  $SO_3$  29.41; found (%): H 0.19; Cl 11.9; K 20.2; Pt 30.1;  $SO_3$  30.0]. Recrystallization from water yielded single crystals. The deuterated compound has also been analogously prepared.

### Crystal data

$K_3[Pt\{(SO_3)_2H\}Cl_2]$ ,  $M_r = 544.43$ , orthorhombic,  $a = 15.134$  (3),  $b = 10.490$  (3),  $c = 7.054$  (1) Å,  $V = 1119.9$  (3) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 3.29$ ,  $D_c = 3.23$  Mg m<sup>-3</sup>,  $F(000) = 999.8$ ,  $\mu(Ag K\alpha) = 7.47$  mm<sup>-1</sup>. The unit-cell parameters were determined by a least-squares refinement from 47 powder reflexions with  $Pb(NO_3)_2$  as an external standard. The parameters of the respective deuterated compound showed no significant deviations from those given above for the hydrogen compound.

The systematic absences  $hkl: h + k = 2n + 1$ , and  $h0l: l = 2n + 1$ , obtained from Weissenberg and precession photographs, indicated the space groups  $Cmcm$ ,  $Cmc2_1$  or  $C2cm$  (=  $Ama2$  rotated). A non-centrosymmetric space group was proposed by intensity statistics.

In order to simplify the absorption correction a sphere with 0.21 mm diameter was ground from a larger crystal fragment.

### Data collection

Three-dimensional intensity data were collected with a PW 1100 four-circle diffractometer in the  $\omega$ -scan mode, using graphite-monochromatized Ag  $K\alpha$  radiation ( $\lambda = 0.5614$  Å). The scan range was  $(0.9 + 0.2 \tan \theta)^\circ$ . With a speed of  $0.1^\circ s^{-1}$  4552 reflexions were measured in the range  $3 \leq \theta \leq 23^\circ$ . Lorentz, polarization and absorption corrections for a sphere were applied; absorption factors were taken from Weber (1969). Estimated standard deviations  $\sigma(F_o)$  for

the  $F_o$ 's have been determined after Hornstra & Stubbe (1972).

Equivalent reflexions were averaged to give 1606 unique reflexions.

### Structure determination and refinement

The crystal structure was solved by the conventional heavy-atom method and refined by a full-matrix least-squares procedure. All calculations were performed with a TR 440 computer using the *SHELX 76* program (Sheldrick, 1976).

The position of the Pt atom was determined from a Patterson map. All other non-hydrogen atoms were located in a Fourier map calculated in  $Cmcm$ . A set of atomic positions was selected according to space group  $Cmc2_1$ . After several cycles of anisotropic refinement even the position of the hydrogen atom could be determined. Complex neutral atomic scattering factors were employed (*International Tables for X-ray Crystallography*, 1974). In the early stages of refinement unit weights were used with convergence at  $R = \sum(|F_o| - |F_c|)/\sum|F_o| = \sum\Delta/\sum|F_o| = 0.0287$ . Later the weighting scheme  $w = 0.503/[\sigma^2(F_o) + 0.00099 \times F_o^2]$  (based on analyses of variance as provided by the *SHELX 76* program) was applied in the refinement leading to final weighted and conventional  $R$  values of  $R_w = \sum w^{1/2} \Delta/\sum w^{1/2} |F_o| = 0.0254$  and  $R = 0.0206$ . The maximum shift of the positional parameters in the last cycle was 0.3 e.s.d.'s with e.s.d. = 0.00024. Refinement of the opposite enantiomorph produced no significant changes in the  $R$  values. The final atomic parameters and equivalent values  $U_{eq}$  of the anisotropic thermal parameters\* are given in Table 1.†

\* Equivalent values  $U_{eq}$  are derived from the anisotropic temperature factors  $U_{ij}$  by the method of Hamilton (1959).

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35497 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates ( $\times 10^4$ ) and equivalent values  $U_{eq}$  ( $\times 10^4$ ) of anisotropic temperature factors, with e.s.d.'s in parentheses

|      | <i>x</i> | <i>y</i>   | <i>z</i> | $U_{eq}$ |
|------|----------|------------|----------|----------|
| Pt   | 0        | 2462.6 (1) | 2500     | 129 (1)  |
| Cl   | 1098 (1) | 1196 (1)   | 4038 (2) | 242 (4)  |
| S    | 1093 (1) | 3484 (1)   | 964 (2)  | 165 (4)  |
| K(1) | 2201 (1) | 3606 (1)   | 6012 (2) | 265 (4)  |
| K(2) | 0        | 1237 (1)   | 7826 (2) | 249 (5)  |
| O(1) | 1882 (2) | 3694 (2)   | 2116 (4) | 219 (9)  |
| O(2) | 1304 (3) | 2726 (4)   | -721 (6) | 346 (11) |
| O(3) | 787 (2)  | 4805 (3)   | 319 (5)  | 335 (10) |
| H    | 0        | 4797 (13)  | 441 (13) | 500 (13) |

### Results and discussion

A projection down the  $c$  axis onto the (001) plane is shown in Fig. 1. The structure is built up of isolated *cis*-dichloro(hydrogendisulfito)platinate(II) anions connected by two sets of crystallographically nonequivalent potassium cations.

#### *The platinum coordination and the trans influence of the sulfito ligand*

Platinum is coordinated by two sulfur and two chlorine atoms in *cis* positions to yield a distorted square (see Fig. 2, which also contains bond lengths and angles). The platinum atom is shifted by 0.086 (1) Å from the plane of the coordinated S and Cl atoms, away from the nearest potassium ion K(2) [distance Pt—K(2) = 3.539 (2) Å]. The Pt—S bond lengths [2.247 (2) Å] seem to be rather short; no other X-ray structure analyses of sulfitoplatinum(II) compounds have been performed, and therefore no comparisons are possible. However, recent structural data for related chloro(dimethyl sulfoxide)platinum(II) complexes are available (Melanson & Rochon, 1975, 1977, 1978*a,b*; Melanson, Hubert & Rochon, 1976). In these compounds the Pt—S bonds vary in the range from 2.19 to 2.24 Å. In addition some Pd—S bond lengths (2.24 to 2.34 Å) in sulfitopalladium(II) compounds are known (Spinnler & Becka, 1967; Capparelli & Becka, 1969; Messer, Breitinge & Haegler, 1979, 1980) and values of the lower limit of this range compare well with the values found in this work. It has been pointed out (Girling & Amma, 1976) that Pd—S and Pt—S bond lengths in analogous palladium(II) and platinum(II) complexes are the same within experimental error (see also Bronger, Günther, Huster & Spangenberg, 1976). The same is true for the metal-ligand bond lengths in other Pd or Pt compounds, e.g.  $K_2PdCl_4$  and  $K_2PtCl_4$  (Mais, Owston & Wood, 1972). In contrast to the short Pt—S bonds the Pt—Cl bonds are remarkably long [2.388 (2) Å] indicating a pronounced structural *trans* influence (for a review see Appleton, Clark & Manzer, 1973) of the sulfito ligand.

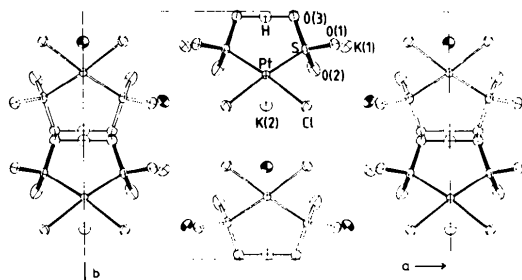


Fig. 1. Projection (ORTEP II; Johnson, 1976) of the structure onto the (001) plane; potassium cations and anions drawn in heavy type and those in light type differ in height by  $c/2$ .

'Normal' terminal Pt—Cl bonds fall in the range from 2.27 to 2.33 Å; examples are  $K_2PtCl_4$  with 2.316 Å (see above), *cis*-Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> with 2.33 Å (Milburn & Truter, 1966), *trans*-Pt(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> with 2.29 Å (Messmer & Amma, 1966) or the above-mentioned chloro(dimethyl sulfoxide)platinum(II) complexes with 2.28 to 2.32 Å (Melanson & Rochon, 1975, 1977, 1978*a,b*; Melanson *et al.*, 1976). On the other hand, phosphine ligands exhibit a strong *trans* influence, similar to that for the sulfito ligand in this work.

Thus, in *cis*-Pt(PMe<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> the (different) Pt—Cl bonds are lengthened to 2.388 (9) Å (Messmer, Amma & Ibers, 1967). So far it is only in *trans*-hydrido-chlorobis(diphenylethylphosphine)platinum(II) [Pt(PEtPh<sub>2</sub>)<sub>2</sub>ClH] that a longer Pt—Cl bond [2.442 (9) Å] has been found (Eisenberg & Ibers, 1965). It is worthwhile noting that the Pt—Cl stretching frequencies of this compound also suggest a *trans* influence similar to that of PMe<sub>3</sub> (*cf.* Appleton *et al.*, 1973).

For the solved sulfitopalladium-complex structures, a *trans* influence is either not obvious (Spinnler & Becka, 1967) or not comparable owing to a special coordination mode of the sulfito ligand (Messer, Breitinge & Haegler, 1979). However, in complexes with at least two sulfite groups *trans* to each other the Pd—S distances are extraordinarily long: 2.294 (6) Å in *trans*-diamminedisulfitopalladate(II) anion [Pd(NH<sub>3</sub>)<sub>2</sub>(SO<sub>3</sub>)<sub>2</sub>]<sup>2-</sup> (Capparelli & Becka, 1969); 2.316 (1) and 2.341 (1) Å in hexasodium tetrasulfitopalladate(II) dihydrate, Na<sub>6</sub>[Pd(SO<sub>3</sub>)<sub>4</sub>]·2H<sub>2</sub>O (Messer, Breitinge & Haegler, 1980). Again, a similar situation is observed for the Pt—P bonds in *trans*-diphosphineplatinum(II) complexes, e.g. *trans*-Pt(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (Messmer & Amma, 1966). Otherwise a structural *trans* influence of the sulfito ligand is documented only in a few cases of octahedral cobalt(III) complexes. The most appropriate example is the pentaamminesulfitocobalt(III) cation (Elder & Trkula, 1974), where the Co—N bond *trans* to the sulfito ligand is significantly longer [2.055 (2) Å] than the *cis* Co—N bonds [average 1.966 (4) Å]. Similar indications have been

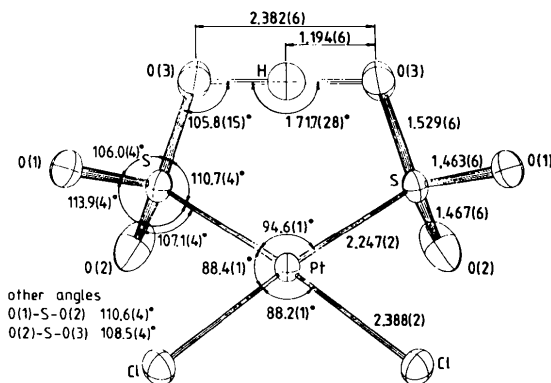


Fig. 2. The anion [Pt(SO<sub>3</sub>)<sub>2</sub>H]Cl<sub>2</sub>]<sup>3-</sup> (ORTEP II; Johnson, 1976).

found in Co<sup>III</sup> complexes with water molecules *trans* to sulfite (Maslen, Raston & White, 1975; Maslen, Raston, White & Yandell, 1975).

#### The sulfite ligand

Distances and angles within the sulfite ligands coordinated through sulfur are contained in Fig. 2. All the angles around the S atoms are tetrahedral to a good approximation, including the Pt–S–O angles. The obvious deviation of the Pt–S–O(1) angle [113.9 (4)°] may be attributed to the strength and relative direction of coordination of O(1) to the general-position potassium K(1).

According to Cruickshank's (1961) theory, the terminal S–O bonds in the present structure are very short (1.46 Å) due to S coordination and enhanced S–O  $\pi$ -bonding as a consequence. On the other hand, the lengthening of the S–O(3) bond seems to be caused by engagement of O(3) in the hydrogen-bond system (see below). The difference in S–O bond lengths is also manifested in the spreading of the S–O valence vibrations over a rather large wave-number range. On the whole, a fairly similar situation has been found in K<sub>2</sub>[Pd(SO<sub>3</sub>)<sub>2</sub>].2H<sub>2</sub>O (Messer, Breiting & Haegler, 1979).

#### The hydrogen bond

Besides the obvious structural *trans* influence of the sulfite group there is another most remarkable feature in this structure, *viz* the unusually short hydrogen bond O(3)⋯H⋯O(3') of 2.382 (6) Å. Up to now only a few examples of comparable short hydrogen bonds have been observed; some of the shortest distances are given in Table 2.

In the present structure the hydrogen bond is expected to be symmetric by space-group symmetry: the most probable position of the hydrogen atom should be on the mirror plane, implying a symmetric single-minimum potential for the hydrogen bond. However, a statistical occupation of two positions correlated by mirror symmetry and hence a symmetric double-minimum potential may not be excluded. It should be pointed out that the hydrogen bond is slightly bent [angle O⋯H⋯O = 171.7 (2.8)°]; but there are no specific attractive or repulsive interactions between the hydrogen and any other atoms which are likely to be responsible for this deviation from linearity.

#### The coordination of potassium

The potassium ions K(2) (site symmetry *m*) are surrounded by two pairs of chlorines and one pair of oxygens O(2) to form a distorted trigonal prism (Fig. 3). Each of these symmetry-correlated pairs of atoms stems from three different anions, *i.e.* K(2) connects three anions with their centers of gravity in the same plane, *e.g.* (100).

In contrast to the quite simple coordination of K(2), the K(1) ions have highly irregular environments, *viz* six oxygens with variable distances and two chlorines, and even two sulfur atoms may be included in the coordination sphere of K(1) (Table 3).

#### The structural arrangement of the lattice constituents

As has been mentioned above each K(2) ion interconnects with three anions in two dimensions by short K(2)⋯O(2) [2.718 (5) Å] and K(2)⋯Cl [3.147 (2) and 3.163 (2) Å] contacts. Thus, this part of

Table 2. *Very short hydrogen-bond systems with distances R(O⋯H⋯O) < 2.40 Å*

| Compound   | R(O⋯H⋯O)<br>(Å)<br>( <i>e.s.d.</i> 's in parentheses) | R(O⋯H)<br>(Å) | Method of<br>determination* | References  |
|--|---|---------------|-----------------------------|---|
| H <sub>3</sub> O <sub>7</sub> <sup>†</sup>                             | 2.29 (2)  | (1.145)‡      | <i>X</i>                    | Abu-Dari, Raymond & Freyberg (1979)   |
| Cu(thiourea) <sub>3</sub><br>hydrogen phthalate                        | 2.351 (9)   | 1.05 (6)      | <i>X</i>                    | Biagini Cingi, Manotti Lanfredi, Tiripicchio & Tiripicchio Camellini (1977) |
| Li hydrogen phthalate  | 2.366 (2)   | 1.163 (9)     | <i>N</i>                    | Bartl & Küppers (1978)  |
|  |   | 1.263 (9)     |                             |   |
|  | 2.385 (2)   | 1.191 (29)    | <i>X</i>                    | Gonschorek & Küppers (1975)   |
|  |   | 1.200 (29)    |                             |   |
| K <sub>3</sub> [Pt{(SO <sub>3</sub> ) <sub>2</sub> H}Cl <sub>2</sub> ] | 2.382 (6)   | 1.194 (6)§    | <i>X</i>                    | This work   |
| CsH(OOCCF <sub>3</sub> ) <sub>2</sub>                                  | 2.38 (3)  | (1.19)‡       | <i>X</i>                    | Golić & Speakman (1965)   |
| Cu hydrogen phthalate  | 2.391 (2)   | 1.108 (4)     | <i>N</i>                    | Bartl & Küppers (1978)  |
|  |   | 1.290 (4)     |                             |   |
| 2,3-Pyridinedicarboxylic<br>acid                                       | 2.398 (3)   | 1.163 (5)     | <i>N</i>                    | Kvick, Koetzle, Thomas & Takusagawa (1974)                                  |
|  |   | 1.238 (5)     |                             |   |
| Di- <i>p</i> -chlorophenyl<br>hydrogen phosphate                       | 2.398 (13)  | —             | <i>X</i>                    | Calleri & Speakman (1964)   |

\* *X* means X-ray and *N* neutron diffraction, respectively.

† In Na<sub>2</sub>[Et<sub>3</sub>MeN][Cr{PhC(S)=N(O)}<sub>3</sub>]. $\frac{1}{2}$ NaH<sub>3</sub>O<sub>2</sub>.18H<sub>2</sub>O.

‡ Linear and symmetric by symmetry restriction.

§ Symmetric by symmetry restriction.

the structure may be understood as a layer parallel to the (100) mirror plane, with the pseudo-squares of the anions perpendicular to this plane. If an analogous arrangement of ideally square disks and cations, both in special positions, is considered (Fig. 4), a layer group  $(b:c) \cdot m : \tilde{c} : \tilde{b}$  results, corresponding to  $pmcb$  (standard setting  $pbam$ ) in international notation (Shubnikov & Koptsik, 1974a). Substitution of more realistic wedge-shaped units for the square disks, and shift of the cations as indicated in Fig. 4, leads to a decrease in symmetry and thus to subgroup  $(b:c) \cdot m \cdot 2_1$ , corresponding to  $pmc2_1$  (translationally equal, index two):

$$(b:c) \cdot m : \tilde{c} : \tilde{b} \cong pmcb \xrightarrow{t(2)} (b:c) \cdot m \cdot 2_1 \cong pmc2_1.$$

Table 3. Interatomic distances (Å) in the environment of the potassium ions K(1)

|           |           |           |           |
|-----------|-----------|-----------|-----------|
| K(1)—O(3) | 2.756 (3) | K(1)—O(1) | 2.977 (3) |
| K(1)—O(1) | 2.792 (4) | K(1)—Cl   | 3.334 (2) |
| K(1)—O(2) | 2.829 (5) | K(1)—Cl   | 3.350 (2) |
| K(1)—O(1) | 2.890 (3) | K(1)—S    | 3.389 (1) |
| K(1)—O(2) | 2.926 (5) | K(1)—S    | 3.484 (1) |

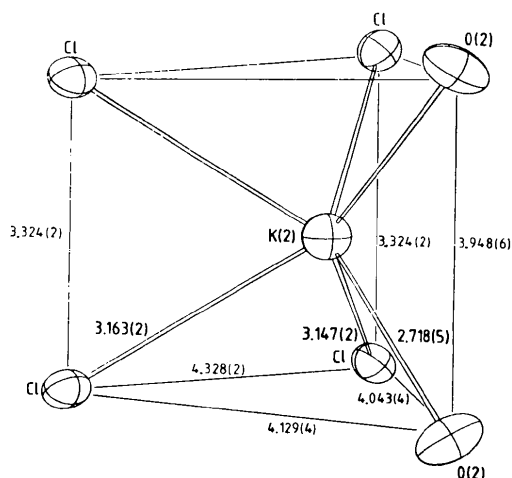


Fig. 3. The environment of the potassium cation K(2).

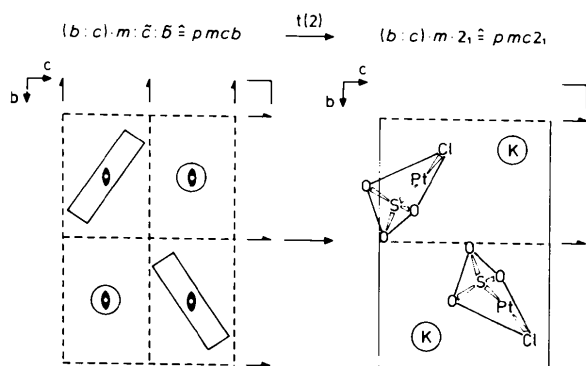


Fig. 4. Symmetry relations between an idealized arrangement of square disks and the real array of wedge-shaped disks in a layer.

Finally, translation of this layer by a vector

$$\frac{a+b}{2}$$

yields the three-dimensional arrangement with space group

$$\left(\frac{a+b}{2} / a:b:c\right) \cdot m \cdot 2_1$$

(non-standard notation) or

$$\left(\frac{a+b}{2} : c:a:b\right) : \tilde{c} \cdot 2_1 \cong Cmc2_1$$

(Shubnikov & Koptsik, 1974b). The connexion between the layers is effected by the K(1) ions. Thus, the crystallographically different K(1) and K(2) ions, in a sense, adopt different functions in the cohesion of the lattice constituents.

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## A Study of the Ordered Structures of the Au–Mn System by High-Voltage–High-Resolution Electron Microscopy.

### I. Two-Dimensional Antiphase Structure of Au<sub>31</sub>Mn<sub>9</sub> Based on the Au<sub>4</sub>Mn Structure

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#### Abstract

A new two-dimensional antiphase structure, Au<sub>31</sub>Mn<sub>9</sub>, was determined directly from high-voltage–high-resolution electron microscopy on a Au–20.7 at.% Mn alloy. The space group is *P4/m* and the unit cell is tetragonal having the lattice constants  $A = \sqrt{10}a$  and  $C = a$ , where  $a \simeq 4.0 \text{ \AA}$  is that of the fundamental f.c.c.

cell. Satisfactory agreement can be obtained between the observed images and the calculations based on the observed images and the calculations based on many-beam dynamical-diffraction theory. The proposed superstructure consists of square-shaped islands of the Au<sub>4</sub>Mn structure of Ni<sub>4</sub>Mo type containing  $3 \times 3$  columns of manganese atoms; the islands are separated by two-dimensional antiphase boundaries parallel to the [310] and  $[\bar{1}30]$  directions of the fundamental f.c.c.