

cation, owing to the lack of ordering of the O2 atoms. Sr₂Bi₂O₅ is a potential oxide ion conductor. The results of the conductivity measurements will be published elsewhere in the near future.

Recently, after this paper's first submission, Torardi, Parise, Santoro, Rawn, Roth & Burton (1991) reported the structure of the low-temperature form of Sr₂Bi₂O₅. In this phase the O-atom vacancies are ordered along [100] with consequent doubling of the *a* axis. The Bi atoms along the chain are not

evenly spaced, thereby contributing to the superstructure effect. In consecutive Bi layers, at a distance of $\frac{1}{2}b$, there are two equally likely ways of vacancy ordering, depending on the position of the *b* glide mirror plane [Fig. 2 (b)]. The glide mirror plane may be situated at $x = \frac{1}{4}$ or at $x = \frac{3}{4}$ of the small cell. In both cases the space group is *Pbmm*. If ordering of vacancies occurs only in the (010) planes, and not between these planes, the overall symmetry is as given in this paper. The ordering described by Torardi, Parise, Santoro, Rawn, Roth & Burton (1991) results in superstructure reflections that are not present in our experiment.

Oxides of the type *A*₂*M*₂O₅ with *A* an alkaline earth and *M* a trivalent ion are relatively rare and are of the perovskite-related brown millerite type, such as Ca₂Fe₂O₅, Sr₂In₂O₅ and Ba₂Tl₂O₅, in which the trivalent ions are half in octahedral and half in tetrahedral coordination. The structure of Sr₂Bi₂O₅ is of a new type.

The authors are indebted to Mr G. H. Renes for the collection of the electron diffraction patterns.

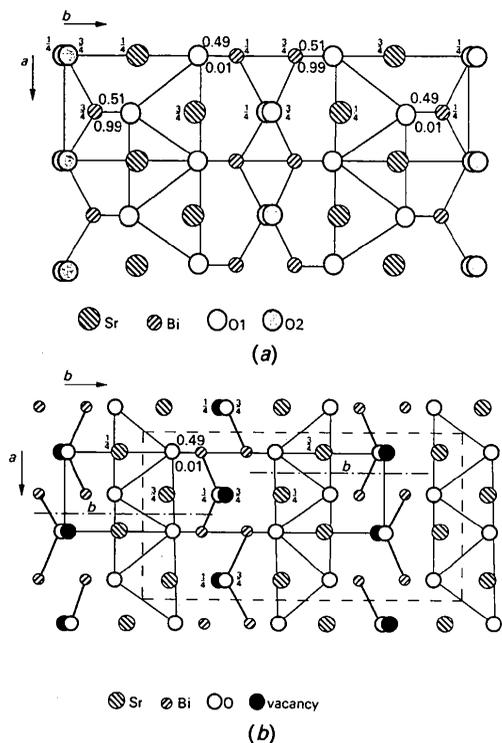


Fig. 2. (a) The structure of Sr₂Bi₂O₅ with space group *Cmc*₂₁. (b) The two possible ways of vacancy ordering in the structure of Sr₂Bi₂O₅. Indicated are the two positions of the *b*-glide mirror plane and the doubled unit cell.

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Acta Cryst. (1992). **C48**, 1382–1386

Structure of Sr₅(BO₃)₃Cl

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(Received 12 July 1991; accepted 13 January 1992)

Abstract. Pentastrontium chloride trisorthoborate, Sr₅(BO₃)₃Cl, *M_r* = 649.98, orthorhombic, *C*222₁, *a* = 10.000 (2), *b* = 14.202 (2), *c* = 7.421 (1) Å, *V* =

1053.9 (3) Å³, *Z* = 4, *D_x* = 4.096 Mg m⁻³, λ(Mo *K*α) = 0.71069 Å, μ = 24.7 mm⁻¹, *F*(000) = 1176, *T* = 295 K, *R* = 0.045 for 911 independent reflections

0108-2701/92/081382-05\$06.00

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with $I > 3\sigma(I)$. The intricate three-dimensional framework consists of several Sr-atom coordination types – SrO_5Cl_2 , SrO_7Cl_2 and SrO_8 – interconnected by sharing either faces, corners, or BO_3 triangles. Each Cl atom is surrounded by six Sr nearest neighbors, forming zigzag chains that propagate along the c axis. The plane of the BO_3 group centered by atom B2 is orthogonal to the twofold rotation b axis, and the vector normal of the BO_3 plane centered by atom B1 is only slightly canted from the 2_1 screw axis, portending a small propensity for optical second-harmonic generation.

Introduction. The utility of photostimulatable luminescence (PSL) for X-ray imaging has generally been confined to binary alkaline-earth halide hosts, *i.e.* $\text{BaFCl}:\text{Eu}^{2+}$ (Takahashi, Kohda, Miyanodai, Kanemitsu, Amitani & Shionoya, 1984), yet several oxide-halide materials have succeeded as effective X-ray storage hosts. For instance, the barium silicate halide $\text{Ba}_5\text{SiO}_4\text{Br}_6$ exhibits comparable optical properties to the now standard halide $\text{BaFCl}:\text{Eu}^{2+}$, yet the incorporated silicate subdues the hygroscopic tendency of alkaline-earth halides (Meijerink & Blasse, 1989). Borates have been shown to be good optical materials for lasers (Schütz, Freitag & Wallenstein, 1990) and second-harmonic generators (Eimerl, Davis, Velsko, Graham & Zalkin, 1987) because of their wide transparency range and high damage thresholds (Velsko, 1988). Therefore, with the introduction of electron-trapping sites, a borate halide should exhibit favorable optical qualities for X-ray storage. A patented prototype already under investigation is Eu^{2+} -doped $A_2B_3O_9X$ ($A = \text{Ca}, \text{Sr}, \text{Ba}$; $X = \text{Cl}, \text{Br}, \text{I}$) (Blasse, Meijerink, Terrell & Neyens, 1988). Considering the recent success of these oxide-halide compounds, the title borate halide was synthesized for optical studies. In addition, initial studies are in progress to investigate its suitability as a second-harmonic generator. Here, we describe the structure of this new material.

Experimental. Powder of $\text{Sr}_5(\text{BO}_3)_3\text{Cl}$ was synthesized from a stoichiometric mixture of $\text{Sr}_3(\text{BO}_3)_2$ [laboratory synthesized by reacting $\text{Sr}(\text{NO}_3)_2$ (ÆSAR, ACS grade) and B_2O_3 (ÆSAR, 99.98%), heating at 1273 K] and SrCl_2 (ÆSAR, 99.9%) heated to 1073 K in a Pt crucible for 8 h. Powder X-ray data collected on an automated Philips diffractometer mimicked the calculated pattern generated with the computer program *LAZY-PULVERIX* (Yvon, Jeitschko & Parthé, 1977) by using the atomic positions determined from the single-crystal refinement presented in this paper. Crystals were grown by slowly cooling a 57.4 SrO:12.9 B_2O_3 :29.7 SrCl_2 mol% melt from 1123 to 1023 K in a Pt

Table 1. *Positional parameters and equivalent isotropic thermal parameters* (Å^2) for $\text{Sr}_5(\text{BO}_3)_3\text{Cl}$

$$B_{\text{eq}} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j.$$

| | x | y | z | B_{eq} |
|-----|------------|-------------|------------|-----------------|
| Sr1 | 0.7605 (2) | 0 | 0 | 0.59 (5) |
| Sr2 | 0.1327 (1) | 0.87145 (9) | 0.9371 (1) | 0.62 (3) |
| Sr3 | \vdots | 0.8651 (1) | \vdots | 0.56 (5) |
| Sr4 | \vdots | 0.1385 (1) | \vdots | 0.63 (6) |
| Cl | 0 | 0.0532 (3) | 0 | 0.9 (1) |
| O1 | 0.508 (1) | 0 | 0 | 0.7 (4) |
| O2 | 0.6712 (8) | 0.8089 (7) | 0.009 (1) | 0.8 (3) |
| O3 | 0.3553 (8) | 0.8007 (7) | 0.986 (1) | 1.0 (3) |
| O4 | 0.6969 (8) | 0.0005 (9) | 0.337 (1) | 1.3 (3) |
| O5 | 0.8817 (9) | 0.8528 (6) | 0.883 (2) | 0.9 (3) |
| B1 | 0.802 (1) | 0.789 (1) | 0.969 (2) | 0.9 (5) |
| B2 | 0.374 (2) | 0 | 0 | 0.2 (2) |

crucible. A colorless crystalline prism ($0.20 \times 0.20 \times 0.15$ mm) was selected for study.

The unit-cell parameters were derived by a least-squares analysis of 20 setting angles in the range $30 < 2\theta < 36^\circ$ that were automatically centered on a Rigaku AFC-6R diffractometer. Intensity data were collected by using ω - 2θ scans with a scan speed of $16^\circ (\omega) \text{ min}^{-1}$ over the angular range $2 \leq 2\theta \leq 70^\circ$ containing the corresponding indices $0 \leq h \leq 16$, $0 \leq k \leq 22$, $0 \leq l \leq 11$. Three standards measured every 300 reflections showed no systematic variation (maximum relative deviation 1.0%), indicating crystalline stability during data collection. The data were corrected for the geometric Lorentz-polarization effects and for secondary extinction with a coefficient of 0.65903×10^{-6} . Of the 1330 measured intensities, 911 unique reflections with $F_o^2 \geq 3\sigma(F_o^2)$ were used in refinement. On the basis of the systematic absences $h + k = 2n + 1$ for hkl , $l = 2n + 1$ for $00l$ and the successful solution and refinement of the structure, the space group was uniquely determined to be $C222_1$.

Calculations were performed on a MicroVAX II computer by using programs from the *TEXSAN* crystallographic software package (Molecular Structure Corporation, 1985). The Sr atoms were located from the results of the direct-methods program *SHELXS86* (Sheldrick, 1985); the remaining atomic positions were determined from subsequent electron density maps. F_c was derived from predetermined neutral scattering factors and corrected for anomalous scattering by using calculated f' and f'' values from *International Tables for X-ray Crystallography* (1974, Vol. IV). After applying an empirical absorption correction (transmission factors: 0.85–1.23) with the program *DIFABS* (Walker & Stuart, 1983) and refining each atom (except B2) with anisotropic thermal parameters, minimization of the function $\sum w(F_o - F_c)^2$ with 83 variables and 911 observations converged to the final residuals $R = 0.045$ and $wR = 0.047$ with $S = 1.38$. The weighting scheme was based on counting statistics [$w = 1/\sigma^2(F_o)$] with $p = 0.05$. The maximum shift/e.s.d. in the last cycle was 0.01.

Table 2. Selected interatomic distances (Å) and angles (°) for Sr₅(BO₃)₃Cl

| | | | |
|------------|-----------|------------|-----------|
| Sr1—Cl × 2 | 3.123 (2) | Sr3—O1 × 2 | 2.669 (1) |
| Sr1—O1 | 2.53 (1) | Sr3—O2 × 2 | 2.70 (1) |
| Sr1—O2 × 2 | 2.858 (9) | Sr3—O3 × 2 | 2.451 (9) |
| Sr1—O4 × 2 | 2.578 (8) | Sr3—O4 × 2 | 2.82 (1) |
| Sr1—O5 × 2 | 2.567 (9) | Sr4—O1 × 2 | 2.705 (2) |
| Sr2—Cl | 3.218 (4) | Sr4—O2 × 2 | 2.586 (9) |
| Sr2—Cl | 2.881 (2) | Sr4—O3 × 2 | 2.58 (1) |
| Sr2—O2 | 2.62 (1) | Sr4—O4 × 2 | 2.86 (1) |
| Sr2—O3 | 2.469 (9) | B1—O2 | 1.37 (2) |
| Sr2—O4 | 2.60 (1) | B1—O3 | 1.42 (2) |
| Sr2—O5 | 2.556 (9) | B1—O5 | 1.36 (2) |
| Sr2—O5 | 2.397 (9) | B2—O1 | 1.34 (2) |
| | | B2—O4 × 2 | 1.40 (1) |
| Cl—Sr1—Cl | 79.82 (6) | O1—Sr3—O1 | 88.20 (6) |
| Cl—Sr1—O2 | 89.7 (2) | O1—Sr3—O2 | 72.4 (3) |
| Cl—Sr1—O4 | 67.3 (2) | O1—Sr3—O3 | 77.7 (3) |
| Cl—Sr1—O5 | 69.0 (2) | O1—Sr3—O4 | 69.6 (3) |
| O1—Sr1—O2 | 71.8 (2) | O1—Sr3—O4 | 51.3 (3) |
| O1—Sr1—O4 | 75.7 (2) | O2—Sr3—O4 | 85.4 (3) |
| O2—Sr1—O4 | 84.4 (3) | O2—Sr3—O3 | 75.8 (3) |
| O2—Sr1—O4 | 86.7 (4) | O2—Sr3—O3 | 91.4 (3) |
| O2—Sr1—O5 | 51.8 (2) | O3—Sr3—O4 | 71.1 (3) |
| O2—Sr1—O4 | 86.7 (4) | O4—Sr3—O4 | 94.7 (4) |
| O4—Sr1—O5 | 77.7 (3) | O1—Sr4—O1 | 86.70 (6) |
| Cl—Sr2—Cl | 81.94 (6) | O1—Sr4—O2 | 73.5 (3) |
| Cl—Sr2—O4 | 89.2 (2) | O1—Sr4—O4 | 68.4 (3) |
| Cl—Sr2—O4 | 65.5 (2) | O1—Sr4—O4 | 50.5 (3) |
| Cl—Sr2—O2 | 107.9 (2) | O1—Sr4—O3 | 74.9 (3) |
| Cl—Sr2—O4 | 65.5 (2) | O2—Sr4—O3 | 93.2 (3) |
| Cl—Sr2—O4 | 105.9 (2) | O2—Sr4—O3 | 75.6 (3) |
| Cl—Sr2—O5 | 73.2 (2) | O2—Sr4—O4 | 84.2 (3) |
| Cl—Sr2—O5 | 68.6 (2) | O3—Sr4—O4 | 71.0 (3) |
| O2—Sr2—O3 | 56.5 (3) | O4—Sr4—O4 | 92.7 (4) |
| O2—Sr2—O5 | 93.8 (3) | O2—B1—O3 | 119 (1) |
| O3—Sr2—O4 | 69.8 (3) | O2—B1—O5 | 122 (1) |
| O3—Sr2—O4 | 74.7 (3) | O3—B1—O5 | 119 (1) |
| O3—Sr2—O5 | 99.0 (3) | O4—B2—O4 | 120 (1) |
| O4—Sr2—O4 | 50.5 (3) | O1—B2—O4 | 120.1 (7) |
| O4—Sr2—O5 | 80.4 (3) | | |
| O5—Sr2—O5 | 77.0 (3) | | |

The final difference electron density map exhibited a maximum peak of $1.48 \text{ e} \text{ \AA}^{-3}$, corresponding to 0.62% of the Sr3 atom peak intensity, and a minimum peak of $-1.99 \text{ e} \text{ \AA}^{-3}$. The atomic positions and interatomic distances and angles are listed in Tables 1 and 2, respectively.*

Discussion. The structure is a complex three-dimensional framework of 7-, 8- and 9-coordinate Sr-centered polyhedra that share O and Cl vertices and BO₃ triangular planes (see Fig. 1). The distorted Sr(1)O₇Cl₂ tricapped trigonal prisms zigzag along the *c* axis *via* corner-sharing Cl atoms. Nona-coordinate Sr centers are common in borates as evidenced by their presence in the compound Sr₃B₂O₆ (Richter & Müller, 1980) and the large oxide family of general formula $A_6MM'(BO_3)_6$, $A = \text{Sr}$ (Thompson, 1991). These prisms also share faces with the distorted Sr(2)O₅Cl₂ tetragonal base-trigonal base polyhedra and with the two crystallographically distinct Sr(3)O₈

* Lists of anisotropic thermal parameters and the observed and calculated structure amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55033 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH0561]

and Sr(4)O₈ square antiprisms. In addition, the SrO₇Cl₂ prisms share two O1—O2—O4 faces with face-condensed Sr(3)O₈ and Sr(4)O₈ antiprisms.

The Sr(2)O₅Cl₂ sites approximate tetragonal base-trigonal base hepta-coordination analogous to the SrO₇ polyhedra found in α -Sr₂Cu(BO₃)₂ (Smith & Keszler, 1989). Their similarity persists with the presence of an additional long Sr—O interaction of 3.014 Å in Sr₅(BO₃)₃Cl that is comparable to a similar weak interaction of 3.11 Å in the strontium copper borate. If this O4 atom is regarded as interacting with atom Sr2, then the local atomic geometry would be an irregular undecahedron. Assuming sevenfold coordination, however, these sites share faces with one another, comprising two Cl atoms and one O atom, and bridge *via* BO₃ triangles to Sr(1)O₇Cl₂ polyhedra.

The antiprisms share mutual O1—O4 rectangular bases in the *ac* plane and adjoin O1—O2—O3 triangular faces in the *ab* plane to form double chains extending in the *c* direction. B2 atoms occupy triangular sites along edges of the rectangular bases, rendering additional coupling of the chains along the *c* axis as illustrated in Fig. 2. The chains are linked to one another, in part, by the bridge atom B1. Each Sr atom is displaced from the mean position between the rectangle of atoms O1 and O4 and the rectangle of atoms O2 and O3. Atoms Sr3 and Sr4 are displaced by 1.87 and 1.84 Å, respectively, from the former rectangle and 0.86 and 0.81 Å, respectively, from the latter. These distortions compare to the square antiprismatic site in β -Sr₂Cu(BO₃)₂, where the span between one plane of O atoms and the central Sr atom is 1.95 Å while the other average distance is 0.90 Å (Smith & Keszler, 1989).

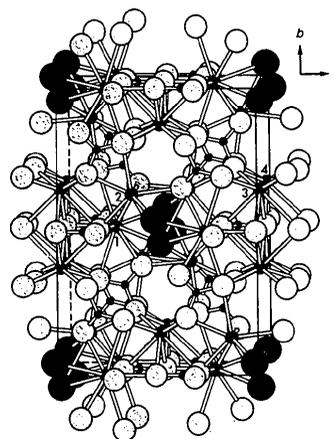


Fig. 1. Schematic unit-cell drawing of Sr₅(BO₃)₃Cl. The small shaded circles represent Sr atoms, the large dark circles represent Cl atoms, the large pale circles represent O atoms, and the small black circles represent B atoms, here, and in Figs. 2 and 3. The four crystallographically distinct Sr atoms are numerically labeled.

The Cl anions are surrounded by six Sr atoms, forming face-sharing distorted octahedral chains along the c axis (Fig. 3). The distortion of the chain can be described as triangular Sr faces alternately canted with respect to the zigzag line of Cl atoms, the deviation observed approximately in the b direction. In contrast, the F atom in $\text{Ca}_5(\text{BO}_3)_3\text{F}$ (Shirong, Qingzhen, Yifan, Aidong & Chuangtian, 1989) is positioned in a distorted tetrahedral environment of Ca atoms, and Mg atoms triangularly surround the central F atom in $\text{Mg}_5(\text{BO}_3)_3\text{F}$ (Brovkin & Nikishova, 1975).

The B1- and B2-centered borate groups are regular with O—B—O bond angles near 120° and average B—O distances of 1.38 (3) Å for B1—O and 1.36 (3) Å for B2—O. The bond angles and distances observed for both BO_3 groups are typical of orthoborates (Shannon & Prewitt, 1968). Because $\text{Sr}_5(\text{BO}_3)_3\text{Cl}$ is not centrosymmetric, it should function as an optical second-harmonic generator.

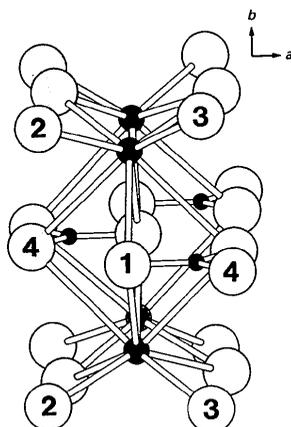


Fig. 2. Sr3- and Sr4-centered distorted square antiprisms in $\text{Sr}_5(\text{BO}_3)_3\text{Cl}$. Atoms are represented as in Fig. 1.

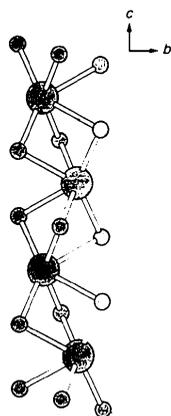


Fig. 3. Chain of Cl-centered distorted octahedra extending along the c screw axis in $\text{Sr}_5(\text{BO}_3)_3\text{Cl}$. Atoms are represented as in Fig. 1.

By applying the free-anionic-group model to the orientations of the orthoborate groups, we have computed the d coefficient for the material. The microscopic hyperpolarizability coefficient for the orthoborate group was taken from Chen, Wu & Li (1990). The coefficient $d_{14}^{2\omega} = 0.101 \text{ pm V}^{-1}$ was then calculated from the structural results of the title compound by assuming each BO_3^{3-} group exhibits D_{3h} symmetry.

$\text{Sr}_5(\text{BO}_3)_3\text{Cl}$ is a thermodynamically stable phase in the $\text{SrO-B}_2\text{O}_3\text{-SrCl}_2$ system with a melting point of 1140 K as determined from differential thermal analysis data from a computer-interfaced Harrop DT 726 thermal analyzer. Two other borate halides represented by the general formula $A_5^{\text{II}}(\text{BO}_3)_3X$ (A = alkaline earth, X = halide) have been reported – $\text{Ca}_5(\text{BO}_3)_3\text{F}$ and $\text{Mg}_5(\text{BO}_3)_3\text{F}$ – but neither compound coincides with the structure of the title compound. The former assumes a monoclinic framework, space group Cm , where the smaller Ca cations prefer distorted octahedral environments. The Mg atoms also adopt a sixfold coordination in $\text{Mg}_5(\text{BO}_3)_3\text{F}$, but this compound orders in the non-centrosymmetric orthorhombic space group $Pna2_1$. In comparison, the larger Sr atoms in the title structure require 7-, 8- and 9-coordinate environments. Despite the increase in cationic coordination number and the associated density decrease in $\text{Sr}_5(\text{BO}_3)_3\text{Cl}$, its extensive face-sharing polyhedra maintain a number density of BO_3 groups per unit cell volume comparable with the lighter cation edge- and corner-sharing $\text{Ca}_5(\text{BO}_3)_3\text{F}$ and $\text{Mg}_5(\text{BO}_3)_3\text{F}$ structures.

This research was supported by the US National Science Foundation, Solid-State Chemistry Program (DMR-88144332). Acknowledgement is made to the Donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. DAK thanks the Alfred P. Sloan Research Foundation for a fellowship, 1989–1991.

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Acta Cryst. (1992). **C48**, 1386–1389

Structure of a Te–Methylene–Te Bridged Double-Butterfly Complex

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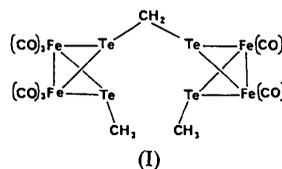
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(Received 12 August 1991; accepted 4 December 1991)

Abstract. *Te,Te'*-Methylenebis[hexacarbonyl- μ -methyltellurio- μ -tellurio-diiron(*Fe—Fe*)], [Fe₂(μ -CH₃-Te)(CO)₆]₂(μ_4 -CH₂Te₂), *M_r* = 1090.01, monoclinic, *C2/c*, *a* = 28.865 (10), *b* = 13.787 (7), *c* = 14.733 (4) Å, β = 104.67 (2)°, *V* = 5671.86 Å³, *Z* = 8, *D_x* = 2.637 Mg m⁻³, $\lambda(\text{Mo } K\alpha)$ = 0.7107 Å, μ = 5.83 mm⁻¹, *F*(000) = 4096, *T* = 296 K. Final *R* and *wR* are 0.0632 and 0.0598, respectively, for 2591 observed reflections. The crystal is stacked with two isomers occupying alternative lattice points. Each lattice point is associated with two identical structures with occupation probabilities of 80 and 20%. One Fe atom [Fe(1)/Fe(3)], and a CO group attached to it, are common in both. For the remaining atoms, a symmetry relationship $1 - x, y, \frac{1}{2} - z$ exists between the positions with unequal probabilities. Each molecule contains two butterfly shaped [(CO)₆Fe₂Te(CH₃)Te] units bridged through a CH₂ group.

Introduction. The dinuclear compound Fe₂(CO)₆(μ -Te₂) is reported as a favourable starting material for the preparation of various mixed-metal complexes (Day, Lesch & Rauchfuss, 1982; Mathur, Mavunkal & Rheingold, 1989). Similarly, the compound Fe₃(CO)₉(μ_3 -Te)₂ also coordinates with the unsaturated metal fragments but it is relatively more inert towards such addition than the diiron compound. The title compound (I), an unusual product, was obtained from the reaction of Fe₃(CO)₉(μ_3 -Te)₂ with excess diazomethane (Mathur, Reddy, Das & Sinha,

1991) at room temperature. Black brick-shaped crystals were obtained from a hexane solution of the compound at 268 K.



Experimental. A crystal of dimensions 0.18 × 0.14 × 0.40 mm was used for the intensity-data collection on a Nicolet *R3m/V* four-circle diffractometer with graphite-monochromated Mo *K*α radiation. The unit-cell parameters were refined from 20 reflections in the range 6 < θ < 13°. A total of 7484 intensities were scanned in the range 2 ≤ 2 θ ≤ 45°, 0 ≤ *h* ≤ 32, 0 ≤ *k* ≤ 15 and -16 ≤ *l* ≤ 16, assuming a primitive monoclinic cell. Two reflections (2,0,10 and 811), checked every 3600 s, indicated no significant variation in intensities. An empirical correction (North, Phillips & Mathews, 1968) for absorption and extinction was applied to all data; minimum and maximum transmission factors were 0.298 and 0.371 respectively. Lp corrections were applied. After averaging the equivalent reflections, 3373 unique reflections (*R*_{int} = 0.076) were obtained which were used in structure determination. The systematic absences (*hkl*: *h* + *k* = 2*n*; *h0l*: *l* = 2*n* + 1 and *h* = 2*n* + 1)