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Stereochemistry of the compounds $[Fe_3(CO)_9XY]$. Crystal and molecular structures of the mixed triiron carbonyl compounds $[Fe_3(CO)_9XY]$ (X, Y = S, Se, or Te)

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Abstract

X-ray analyses of $[Fe_3(CO)_9SSe]$, $[Fe_3(CO)_9STe]$ and of $[Fe_3(CO)_9SeTe]$ was performed. The three compounds are isomorphous and belong to the triclinic space group $P\bar{1}$ with a = 6.835(1), 6.996(1), 6.964(1) Å, b = 9.186(2), 9.367(1), 9.360(2) Å, c = 13.121(3), 13.058(2); 13.189(2) Å, α = 93.79(3), 93.23(1), 94.09(2)°, β = 94.21(3), 94.03(1), 94.54(2)°, γ = 110.89(3), 111.14(1), 110.67(2)° for the SSe, STe and SeTe complexes, respectively. The structures were refined anisotropically to R = 0.026, 0.042, 0.030 for 3127, 3465, 2564 observed reflections for the SSe, STe and SeTe complexes, respectively. They belong to the well known series of $[Fe_3(CO)_9XY]$ complexes formed by an open triangle of iron atoms each linked to three terminal CO groups, with two faces capped by a chalcogen atom. The bond distances and angles of these mixed complexes are well within the ranges imposed due to the different dimensions of the chalcogen atoms. Intermolecular contacts occur when at least one chalcogen atom is tellurium. Examining some relevant geometrical features of the complexes with X,Y = S, Se, Te, NR, PR, AsR..., a regular trend of the Fe–Fe distances is found, depending on the dimensions of the capping atoms; an asymmetry of the Fe–Fe distances is attributed to steric factors.

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1. Introduction

A great number of complexes with the formula $[Fe_3(CO)_9XY]$ have the basic geometry of an open triangle of iron atoms capped on both faces by two moieties donating a total of eight electrons (4 + 4 (S, Se, Te, NR, AsR,) or 5 + 3 (OR, CR)) according to Wade's rules, which give these complexes a nido-octahedral structure.

The mixed compounds $[Fe_3(CO)_9XY]$ (X, Y = S, Se, or Te) belong to this class of cluster and were prepared and kinetically studied some years ago [1]. Recently [2] some reactions of $[Fe_3(CO)_9STe]$ were studied and now single-crystal X-ray analyses of $[Fe_3(CO)_9SSe]$, $Fe_3(CO)_9STe]$, and $[Fe_3(CO)_9SeTe]$ have been carried out. A comparison with other complexes of the class is made.

2. Results and discussion

Figures 1, 2 and 3 show the molecular structrures of the three isomorphous compounds viewed along three different axes and in Table 1 the bond distances and angles are collected.

The structures are formed by an open triangle of iron atoms capped on both faces by a chalcogen atom; each iron atom binds three terminal carbonyl groups and the ideal non-crystallographic molecular symmetry is *Cs* with a pseudomirror plane through XYFe(2) (more evident in Fig. 2). The structures are isomorphous with $[Fe_3(CO)_9S_2]$ [3b], $[Fe_3(CO)_9Se_2]$ [4], $[Fe_3(CO)_9Te_2]$ [5], $[Os_3(CO)_9S_2]$ [6], and $[Fe_2Ru(CO)_9S_2]$ [7] ($P\bar{1}$, a = 6.803(3), b = 9.285(4), c = 13.154(5) Å, α = 93.71(4), β = 96.53(5), γ = 110.72(3)°).

These mixed structures are disordered with respect to the Fe_3 plane with the superposition of the two structures with different occupancy factors (see Experimental section); in the STe and SSe structures, there is a great preponderance of one of the two orientations, but in the SeTe compound the ratio is 60:40.

The Fe–X, Y distances reflect this disorder and are always longer (Fe–S in $[Fe_3(CO)_9SSe]$ (2.290 Å), $[Fe_3(CO)_9STe]$ (2.283 Å) and Fe–Se in $[Fe_3(CO)_9SeTe]$ (2.437 Å)) or shorter (Fe–Se in $[Fe_3(CO)_9SSe]$ (2.351

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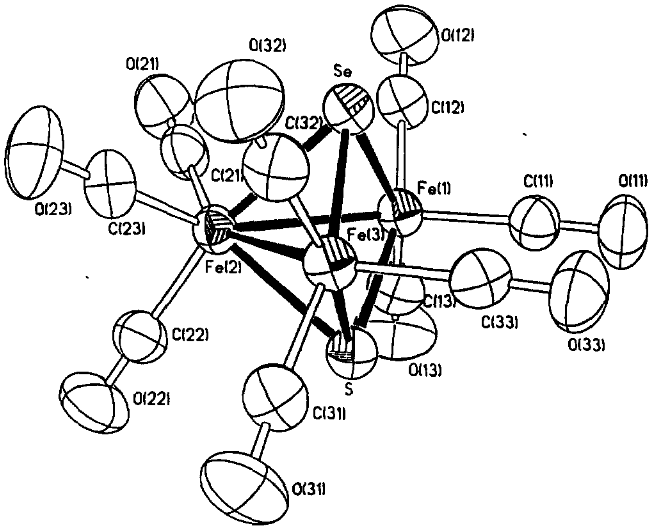


Fig. 1. Molecular structure of [Fe$_3$(CO)$_9$SSe] with thermal ellipsoids (50% of probability) and the atom-labelling scheme.

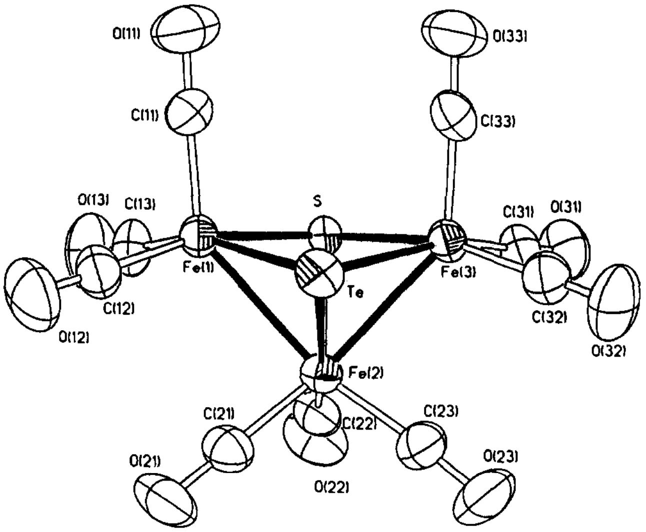


Fig. 3. Molecular structure of [Fe$_3$(CO)$_9$SeTe] with thermal ellipsoids (50% of probability) and the atom labelling scheme.

Å), Fe–Te in [Fe$_3$(CO)$_9$STe] (2.533 Å) and in [Fe$_3$(CO)$_9$SeTe] (2.480 Å)) than the values found in [Fe$_3$(CO)$_9$S$_2$], [Fe$_3$(CO)$_9$Se$_2$] and [Fe$_3$(CO)$_9$Te$_2$] (2.240$_{av}$ Å, 2.35$_{av}$ Å and 2.538$_{av}$ Å) [3–5].

All the parameters which are supposed to depend on the S, Se, Te substitution have for the mixed compounds intermediate values compared to those in the S$_2$, Se$_2$ and Te$_2$ complexes: *e.g.*, the Fe–Fe distances and the Fe(1)–Fe(2)–Fe(3) angles show an increase along the S$_2$, SSe, Se$_2$, STe, SeTe, Te$_2$ sequence (Table 2).

In all three mixed compounds, there is always an Fe–Fe distance significantly (13–18σ) longer than the other one, and the Fe(2)–X, Y distance is also longer than the other two, with a consequent flattening of the Fe$_2$XY rhombus.

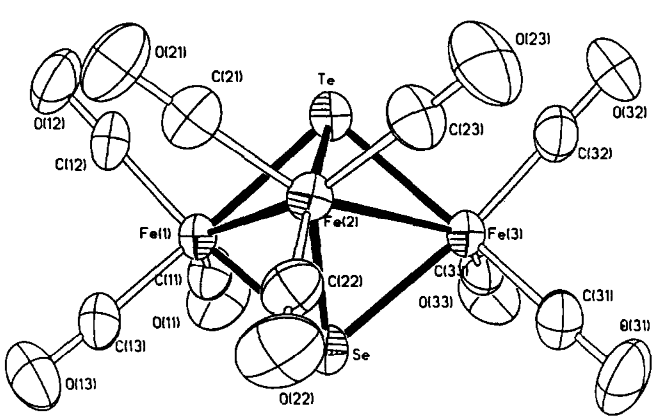


Fig. 2. Molecular structure of [Fe$_3$(CO)$_9$STe] with thermal ellipsoids (50% of probability) and the atom labelling scheme.

The two Fe(1), Fe(3) iron atoms bind three terminal CO groups, two chalcogen atoms and one iron atom in a distorted octahedral coordination, while the unique Fe(2) atom has heptacoordination, with a 3:4 arrangement of three bonds to the CO groups and four bonds to the Fe$_2$XY group.

For 3:4 coordination, two geometries are possible when all the ligands are equal, the staggered and the eclipsed conformations. A rotation of nearly 15° is required to pass from one to the other.

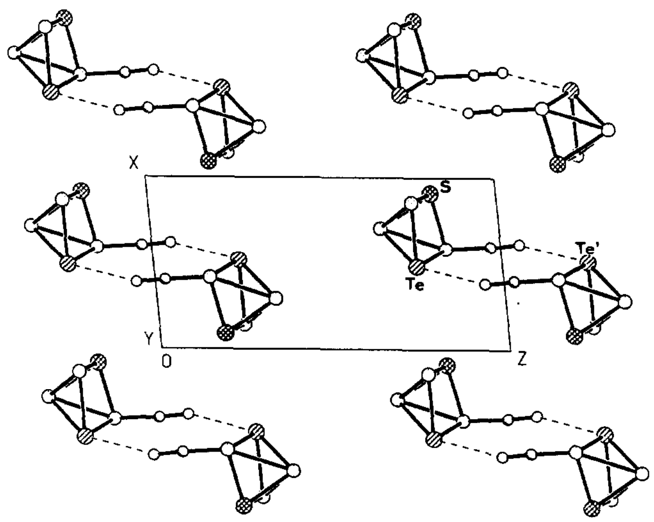


Fig. 4. View of the intermolecular contacts smaller than the sum of the Van der Waals radii in [Fe$_3$(CO)$_9$STe]. The CO groups not involved in the intermolecular contacts are omitted for clarity. The atoms without the prime refer to the molecule at x, y, z, with the prime to the molecule related by a centre of symmetry.

TABLE 1. Bond angles (°) and bond lengths (Å)

[Fe$_3$(CO)$_9$SSe]			
Fe(2)-Fe(1)-S	55.4(1)	Se-Fe(2)-C(23)	93.8(1)
Fe(2)-Fe(1)-Se	56.7(1)	C(21)-Fe(2)-C(23)	100.2(1)
S-Fe(1)-Se	83.0(1)	C(22)-Fe(2)-C(23)	93.6(1)
Fe(2)-Fe(1)-C(11)	141.9(1)	Fe(2)-Fe(3)-S	55.2(1)
S-Fe(1)-C(11)	96.2(1)	Fe(2)-Fe(3)-Se	56.5(1)
Se-Fe(1)-C(11)	99.0(1)	S-Fe(3)-Se	83.0(1)
Fe(2)-Fe(1)-C(12)	109.8(1)	Fe(2)-Fe(3)-C(31)	107.9(1)
S-Fe(1)-C(12)	165.1(1)	S-Fe(3)-C(31)	90.9(1)
Se-Fe(1)-C(12)	89.6(1)	Se-Fe(3)-C(31)	163.8(1)
C(11)-Fe(1)-C(12)	97.8(1)	Fe(2)-Fe(3)-C(32)	110.5(1)
Fe(2)-Fe(1)-C(13)	106.4(1)	S-Fe(3)-C(32)	165.6(1)
S-Fe(1)-C(13)	91.1(1)	Se-Fe(3)-C(32)	90.4(1)
Se-Fe(1)-C(13)	162.3(1)	C(31)-Fe(3)-C(32)	92.1(1)
C(11)-Fe(1)-C(13)	98.2(1)	Fe(2)-Fe(3)-C(33)	141.2(1)
C(12)-Fe(1)-C(13)	92.1(1)	S-Fe(3)-C(33)	95.8(1)
Fe(1)-Fe(2)-Fe(3)	82.0(1)	Se-Fe(3)-C(33)	98.8(1)
Fe(1)-Fe(2)-S	55.0(1)	C(31)-Fe(3)-C(33)	96.7(1)
Fe(3)-Fe(2)-S	54.8(1)	C(32)-Fe(3)-C(33)	97.8(1)
Fe(1)-Fe(2)-Se	55.9(1)	Fe(1)-S-Fe(2)	69.5(1)
Fe(3)-Fe(2)-Se	55.8(1)	Fe(1)-S-Fe(3)	97.5(1)
S-Fe(2)-Se	82.3(1)	Fe(2)-S-Fe(3)	69.9(1)
Fe(1)-Fe(2)-C(21)	82.1(1)	Fe(1)-Se-Fe(2)	67.4(1)
Fe(3)-Fe(2)-C(21)	150.2(1)	Fe(1)-Se-Fe(3)	94.3(1)
S-Fe(2)-C(21)	130.2(1)	Fe(2)-Se-Fe(3)	67.8(1)
Se-Fe(2)-C(21)	94.5(1)	Fe(1)-C(11)-O(11)	177.9(2)
Fe(1)-Fe(2)-C(22)	116.7(1)	Fe(1)-C(12)-O(12)	178.9(3)
Fe(3)-Fe(2)-C(22)	116.2(1)	Fe(1)-C(13)-O(13)	177.9(3)
S-Fe(2)-C(22)	85.7(1)	Fe(2)-C(21)-O(21)	177.5(3)
Se-Fe(2)-C(22)	168.1(1)	Fe(2)-C(22)-O(22)	179.6(3)
C(21)-Fe(2)-C(22)	93.5(1)	Fe(2)-C(23)-O(23)	177.6(3)
Fe(1)-Fe(2)-C(23)	149.6(1)	Fe(3)-C(31)-O(31)	177.3(3)
Fe(3)-Fe(2)-C(23)	81.6(1)	Fe(3)-C(32)-O(32)	179.8(3)
S-Fe(2)-C(23)	129.6(1)	Fe(3)-C(33)-O(33)	176.9(3)
Fe(1)-Fe(2)	2.614(1)	Fe(3)-Se	2.346(1)
Fe(1) · · · Fe(3)	3.438(1)	Fe(3)-C(31)	1.811(3)
Fe(1)-S	2.286(1)	Fe(3)-C(32)	1.822(3)
Fe(1)-Se	2.342(1)	Fe(3)-C(33)	1.784(3)
Fe(1)-C(11)	1.777(3)	S · · · Se	3.069(1)
Fe(1)-C(12)	1.809(2)	C(11)-O(11)	1.140(4)
Fe(1)-C(13)	1.815(3)	C(12)-O(12)	1.129(3)
Fe(2)-Fe(3)	2.627(1)	C(13)-O(13)	1.124(4)
Fe(2)-S	2.297(1)	C(21)-O(21)	1.135(3)
Fe(2)-Se	2.365(1)	C(22)-O(22)	1.124(4)
Fe(2)-C(21)	1.801(2)	C(23)-O(23)	1.145(4)
Fe(2)-C(22)	1.805(3)	C(31)-O(31)	1.125(3)
Fe(2)-C(23)	1.786(3)	C(32)-O(32)	1.130(4)
Fe(3)-S	2.286(1)	C(33)-O(33)	1.130(4)
[Fe$_3$(CO)$_9$STe]			
Fe(2)-Fe(1)-S	54.6(1)	Te-Fe(2)-C(23)	95.2(3)
Fe(2)-Fe(1)-Te	59.1(1)	C(21)-Fe(2)-C(23)	100.2(3)
S-Fe(1)-Te	83.8(1)	C(22)-Fe(2)-C(23)	93.8(4)
Fe(2)-Fe(1)-C(11)	142.7(2)	Fe(2)-Fe(3)-S	54.3(1)
S-Fe(1)-C(11)	96.6(2)	Fe(2)-Fe(3)-Te	58.8(1)
Te-Fe(1)-C(11)	98.5(3)	S-Fe(3)-Te	83.5(1)
Fe(2)-Fe(1)-C(12)	109.5(2)	Fe(2)-Fe(3)-C(31)	106.8(2)
S-Fe(1)-C(12)	164.1(2)	S-Fe(3)-C(31)	90.8(2)
Te-Fe(1)-C(12)	88.7(2)	Te-Fe(3)-C(31)	165.0(2)
C(11)-Fe(1)-C(12)	98.4(3)	Fe(2)-Fe(3)-C(32)	111.4(2)
Fe(2)-Fe(1)-C(13)	103.1(3)	S-Fe(3)-C(32)	165.6(2)
S-Fe(1)-C(13)	90.4(2)	Te-Fe(3)-C(32)	90.3(2)
Te-Fe(1)-C(13)	161.3(3)	C(31)-Fe(3)-C(32)	91.9(3)

TABLE 1 (continued)

[Fe$_3$(CO)$_9$STe]			
C(11)–Fe(1)–C(13)	99.9(4)	Fe(2)–Fe(3)–C(33)	140.0(2)
C(12)–Fe(1)–C(13)	92.3(3)	S–Fe(3)–C(33)	95.2(2)
Fe(1)–Fe(2)–Fe(3)	83.5(1)	Te–Fe(3)–C(33)	96.5(2)
Fe(1)–Fe(2)–S	54.3(1)	C(31)–Fe(3)–C(33)	97.8(3)
Fe(3)–Fe(2)–S	54.1(1)	C(32)–Fe(3)–C(33)	98.5(3)
Fe(1)–Fe(2)–Te	57.8(1)	Fe(1)–S–Fe(2)	71.0(1)
Fe(3)–Fe(2)–Te	57.8(1)	Fe(1)–S–Fe(3)	102.1(1)
S–Fe(2)–Te	82.8(1)	Fe(2)–S–Fe(3)	71.6(1)
Fe(1)–Fe(2)–C(21)	83.9(2)	Fe(1)–Te–Fe(2)	63.1(1)
Fe(3)–Fe(2)–C(21)	149.2(3)	Fe(1)–Te–Fe(3)	89.3(1)
S–Fe(2)–C(21)	133.5(2)	Fe(2)–Te–Fe(3)	63.5(1)
Te–Fe(2)–C(21)	91.8(3)	Fe(1)–C(11)–O(11)	176.8(6)
Fe(1)–Fe(2)–C(22)	112.8(2)	Fe(1)–C(12)–O(12)	178.0(7)
Fe(3)–Fe(2)–C(22)	117.5(2)	Fe(1)–C(13)–O(13)	176.3(8)
S–Fe(2)–C(22)	86.3(2)	Fe(2)–C(21)–O(21)	178.8(7)
Te–Fe(2)–C(22)	168.6(2)	Fe(2)–C(22)–O(22)	179.2(5)
C(21)–Fe(2)–C(22)	93.3(3)	Fe(2)–C(23)–O(23)	177.1(6)
Fe(1)–Fe(2)–C(23)	152.9(3)	Fe(3)–C(31)–O(31)	176.9(7)
Fe(3)–Fe(2)–C(23)	79.5(2)	Fe(3)–C(32)–O(32)	179.7(6)
S–Fe(2)–C(23)	126.2(2)	Fe(3)–C(33)–O(33)	178.2(6)
Fe(1)–Fe(2)	2.654(1)	Fe(3)–Te	2.527(1)
Fe(1) ··· Fe(3)	3.546(1)	Fe(3)–C(31)	1.809(6)
Fe(1)–S	2.279(1)	Fe(3)–C(32)	1.820(8)
Fe(1)–Te	2.517(1)	Fe(3)–C(33)	1.772(7)
Fe(1)–C(11)	1.768(6)	S ··· Te	3.208(1)
Fe(1)–C(12)	1.820(6)	C(11)–O(11)	1.144(8)
Fe(1)–C(13)	1.812(9)	C(12)–O(12)	1.100(8)
Fe(2)–Fe(3)	2.672(1)	C(13)–O(13)	1.139(12)
Fe(2)–S	2.289(1)	C(21)–O(21)	1.148(7)
Fe(2)–Te	2.554(1)	C(22)–O(22)	1.111(11)
Fe(2)–C(21)	1.784(5)	C(23)–O(23)	1.148(10)
Fe(2)–C(22)	1.812(8)	C(31)–O(31)	1.142(8)
Fe(2)–C(23)	1.775(7)	C(32)–O(32)	1.126(11)
Fe(3)–S	2.282(2)	C(33)–O(33)	1.151(8)
[Fe$_3$(CO)$_9$SeTe]			
Fe(2)–Fe(1)–Te	57.7(1)	Se–Fe(2)–C(23)	128.5(1)
Fe(2)–Fe(1)–Se	56.7(1)	C(21)–Fe(2)–C(23)	100.4(2)
Te–Fe(1)–Se	84.0(1)	C(22)–Fe(2)–C(23)	94.6(3)
Fe(2)–Fe(1)–C(11)	142.6(2)	Fe(2)–Fe(3)–Te	57.5(1)
Te–Fe(1)–C(11)	99.2(2)	Fe(2)–Fe(3)–Se	56.4(1)
Se–Fe(1)–C(11)	95.0(2)	Te–Fe(3)–Se	83.9(1)
Fe(2)–Fe(1)–C(12)	109.5(2)	Fe(2)–Fe(3)–C(31)	106.8(2)
Te–Fe(1)–C(12)	88.9(2)	Te–Fe(3)–C(31)	163.6(2)
Se–Fe(1)–C(12)	166.2(2)	Se–Fe(3)–C(31)	90.8(2)
C(11)–Fe(1)–C(12)	97.9(2)	Fe(2)–Fe(3)–C(32)	110.3(1)
Fe(2)–Fe(1)–C(13)	104.6(2)	Te–Fe(3)–C(32)	89.8(1)
Te–Fe(1)–C(13)	161.6(2)	Se–Fe(3)–C(32)	166.6(1)
Se–Fe(1)–C(13)	90.2(2)	C(31)–Fe(3)–C(32)	92.1(2)
C(11)–Fe(1)–C(13)	98.8(3)	Fe(2)–Fe(3)–C(33)	141.2(2)
C(12)–Fe(1)–C(13)	92.8(2)	Te–Fe(3)–C(33)	98.4(1)
Fe(1)–Fe(2)–Fe(3)	84.9(1)	Se–Fe(3)–C(33)	94.2(2)
Fe(1)–Fe(2)–Te	56.8(1)	C(31)–Fe(3)–C(33)	97.5(2)
Fe(3)–Fe(2)–Te	56.6(1)	C(32)–Fe(3)–C(33)	98.3(2)
Fe(1)–Fe(2)–Se	56.4(1)	Fe(1)–Te–Fe(2)	65.5(1)
Fe(3)–Fe(2)–Se	56.3(1)	Fe(1)–Te–Fe(3)	94.7(1)
Te–Fe(2)–Se	83.3(1)	Fe(2)–Te–Fe(3)	65.9(1)
Fe(1)–Fe(2)–C(21)	80.8(2)	Fe(1)–Se–Fe(2)	66.9(1)
Fe(3)–Fe(2)–C(21)	149.2(2)	Fe(1)–Se–Fe(3)	96.6(1)
Te–Fe(2)–C(21)	92.9(2)	Fe(2)–Se–Fe(3)	67.3(1)
Se–Fe(2)–C(21)	131.1(2)	Fe(1)–C(11)–O(11)	178.8(4)
Fe(1)–Fe(2)–C(22)	115.2(2)	Fe(1)–C(12)–O(12)	178.6(5)

TABLE 1 (continued)

$[Fe_3(CO)_9SeTe]$			
Fe(3)-Fe(2)-C(22)	117.1(1)	Fe(1)-C(13)-O(13)	177.9(5)
Te-Fe(2)-C(22)	168.6(2)	Fe(2)-C(21)-O(21)	177.0(5)
Se-Fe(2)-C(22)	85.3(1)	Fe(2)-C(22)-O(22)	178.1(5)
C(21)-Fe(2)-C(22)	93.6(2)	Fe(2)-C(23)-O(23)	176.6(5)
Fe(1)-Fe(2)-C(23)	150.1(2)	Fe(3)-C(31)-O(31)	176.6(5)
Fe(3)-Fe(2)-C(23)	79.2(2)	Fe(3)-C(32)-O(32)	178.0(5)
Te-Fe(2)-C(23)	93.4(2)	Fe(3)-C(33)-O(33)	178.2(5)
Fe(1)-Fe(2)	2.686(1)	Fe(3)-Se	2.436(1)
Fe(1) ··· Fe(3)	3.635(1)	Fe(3)-C(31)	1.811(5)
Fe(1)-Te	2.471(1)	Fe(3)-C(32)	1.804(6)
Fe(1)-Se	2.433(1)	Fe(3)-C(33)	1.780(5)
Fe(1)-C(11)	1.772(5)	Se ··· Te	3.282(1)
Fe(1)-C(12)	1.803(5)	C(11)-O(11)	1.132(7)
Fe(1)-C(13)	1.806(6)	C(12)-O(12)	1.126(6)
Fe(2)-Fe(3)	2.702(1)	C(13)-O(13)	1.140(8)
Fe(2)-Te	2.497(1)	C(21)-O(21)	1.143(6)
Fe(2)-Se	2.441(1)	C(22)-O(22)	1.123(8)
Fe(2)-C(21)	1.783(4)	C(23)-O(23)	1.137(7)
Fe(2)-C(22)	1.803(6)	C(31)-O(31)	1.127(6)
Fe(2)-C(23)	1.783(5)	C(32)-O(32)	1.151(8)
Fe(3)-Te	2.472(1)	C(33)-O(33)	1.134(6)

In the complexes $[Fe_3(CO)_9XY]$ the tetraatomic core is formed by Fe_2XY and the number of possible geometries increases if $X \neq Y$. All the known structures containing this core fall into three groups with a CO of the $Fe_{unique}(CO)_3$ group eclipsing the Fe (type a), or the X or Y atom (type b), or staggered (type c) according to Scheme 1.

No distinction of the staggered forms is possible due to the very small rotations involved, and to the impossibility of differentiating between the conformers.

The mixed (SSe, STe, SeTe) complexes belong to class (b). Table 2, where all the known $Fe_3(CO)_9XY$ structures are grouped, shows a prevalence of the eclipsed forms (a) and (b). The general distribution of these conformations is not dependent on X and Y even though type (c) is shown only by the most bulky X, Y substituents (the converse does not hold). Furthermore, in some cases two different conformations are present for the same compound in different matrices (*e.g.* $[Fe_3(CO)_9S_2]$ [3a] alone is of type (b) and co-crystallized with $[Fe_2(CO)_6S_2]$ [3b] it is of type (a)). Two crystallographically independent molecules may occur in the same crystal [18]. In no case are there intermolecular contacts shorter than the sum of the Van der Waals radii that could justify the preference of one conformer over the others.

Considering homogeneous groups of compounds, Table 2 shows a regular increase of the Fe–Fe distances with increasing covalent radii of X, Y; a similar increase of the $Fe–Fe_{unique}–Fe$ angles occurs, even if proportionately less. The X ··· Y distances inside the Fe_3XY clusters are always smaller than the sum of the Van der Waals radii. Table 2 also suggests that the complexes $[Fe_3(CO)_9XY]$ show a systematic asymmetry of the two Fe–Fe bonds. The difference ranges from 4σ to 60σ, although the small differences are less significant because they correspond, in most cases, to the largest σ's in the atomic coordinates.

These differences may be due to steric or to electronic factors, which are not easily discernible. However, the largest differences ($50–60\sigma$) correspond to structures of type (a), in which the Fe–Fe bonds have

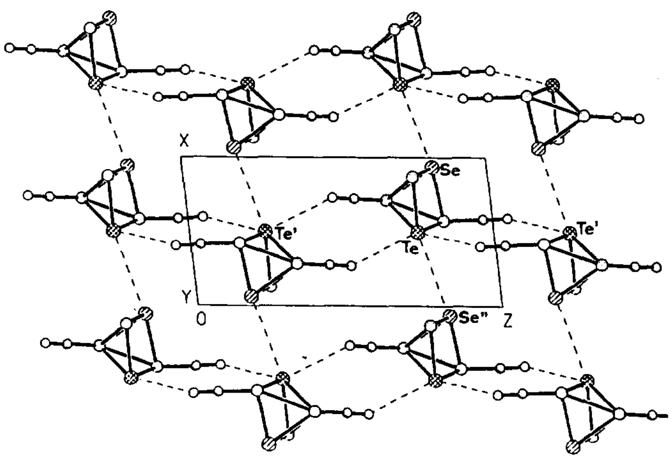
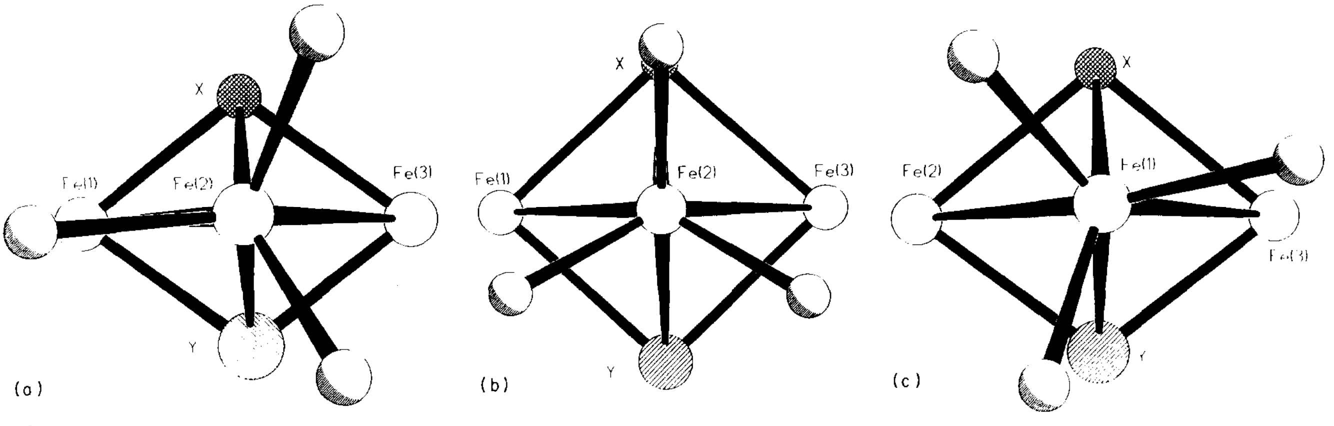


Fig. 5. View of the intermolecular contacts smaller than the sum of the Van der Waals radii in $[Fe_3(CO)_9SeTe]$. The CO groups not involved in the contacts are omitted for clarity. The atoms without the prime belong to the molecule at *x*, *y*, *z*, with one prime to the molecule related by a centre of symmetry, with the double prime to the molecule at 1-*x*, *y*, *z*.

TABLE 2. Some relevant data of the [$Fe_3(CO)_9XY$] complexes

Compound	Fe–Fe	Fe $\cdots$ Fe	Fe–Fe–Fe	Type	X $\cdots$ Y	Ref.
[$Fe_2(CO)_9(\mu_3\text{-}S)_2$]	2.595(1) 2.599(1)	3.373(1)	81.0(1)	b	2.893	3a
	2.582(9) 2.609(10)	3.37(1)		a	2.86(2)	3b
[$Fe_3(CO)_9(\mu_3\text{-}Se)_2$]	2.64(2) 2.66(2)	3.51(2)		b	3.10(2)	4
[$Fe_3(CO)_9(\mu_3\text{-}Te)_2$]	2.740(1) 2.754(1)	3.774(1)	86.8(1)	b	3.380(1)	5
[$Fe_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}SO)$]	2.623(1) 2.647(1)				2.72	8
[$Fe_2(CO)_9(\mu_3\text{-}CMe)(\mu_3\text{-}OMe)_3$]	2.459(3) 2.472(3)	3.059(4)		b	2.376	9
[$Fe_3(CO)_9(\mu_3\text{-}NPh)_2$]	2.421(1) 2.484(1)		76.7(1)	a	2.301(6)	10
[$Fe_3(CO)_9(\mu_3\text{-}NMe)_2$]	2.436(7) 2.488(7)	3.044(8)	76.4(2)	a	2.24(2)	11
[$Fe_3(CO)_9(\mu_3\text{-}N_2CPh_2)_2$]	2.43 2.46	3.06				12
[$Fe_3(CO)_9(\mu_3\text{-}PMes)_2$ [a]	2.632(3) 2.721(2)	3.566(3)	83.5(1)		2.653	13
[$Fe_3(CO)_9(\mu_3\text{-}PPh)_2$]	2.718(3) 2.717(3)	3.554(3)	81.7(1)	a	2.587(5)	14
	2.714(3) 2.717(3)	3.533(3)	81.2(1)	a		
[$Fe_3(CO)_9(\mu_3\text{-}AsPh)_2$]	2.752(2) 2.796(2)	3.705(2)	83.8(5)	b	2.791(2)	15
[$Fe_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}NC_6H_4CH_3)$]	2.50(1) 2.52(1)	3.19(1)	78.8(2)	c	2.6(1)	16
	2.51(1) 2.53(1)	3.19(1)	78.2(1)	c	2.6(1)	
[$Fe_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}PC_6H_4OMe)$]	2.634(1) 2.686(1)	3.499(1)	82.23(2)	c	2.730(2)	17
[$Fe_3(CO)_9(\mu_3\text{-}SW(CO)_5)(\mu_3\text{-}P\text{-}{}^tBu)$]	2.654(5) 2.677(4)	3.488(6)	81.7(1)	b	2.747(8)	18
[$Fe_3(CO)_9(\mu_3\text{-}SCr(CO)_5)(\mu_3\text{-}P\text{-}{}^tBu)$]	2.652(4) 2.696(4)	3.501(5)	81.8(1)	b	2.762(6)	18
[$Fe_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}PPh)$]	2.664(2) 2.666(1)	3.499(1)	82.05(4)	b	2.729(2)	17
	2.652(1) 2.660(1)	3.511(1)	82.75(2)	c	2.714(1)	
[$Fe_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}PPh)$]	2.664(2) 2.646(5)	3.511(6)	82.8(1)	b	2.713(5)	19
	2.650(3) 2.640(3)	3.516(6)	83.3(1)	b	2.696(5)	
	2.668(3) 2.642(3)	3.487(6)	82.1(1)	b	2.738(5)	
[$Fe_3(CO)_9((\mu_3\text{-}S)(\mu_3\text{-}AsPh)$]	2.667(3) 2.679(3)	3.550(3)	83.2(1)	b	2.816(3)	19
	2.658(3) 2.668(3)	3.556(3)	84.1(1)	c	2.799(3)	
[$Fe_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}Se)$]	2.614(1) 2.627(1)	3.438(1)	82.0(1)	b	3.069(1)	[b]
[$Fe_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}Te)$]	2.654(1) 2.672(1)	3.546(1)	83.5(1)	b	3.208(1)	[b]
[$Fe_2(CO)_9(\mu_3\text{-}Se)(\mu_3\text{-}Te)$]	2.686(1) 2.702(1)	3.635(1)	84.9(1)	b	3.282(1)	[b]

[a] Mes = 2, 4, 6-$Me_3C_6H_2$. [b] This work.



Scheme 1.

different environments. In Scheme 1 (a), the CO group eclipsing the Fe atom gives rise to a short CO ··· Fe(1) contact (about 2.7 Å), while the other two CO groups have longer distances (about 3.4 Å for C_{CO} ··· Fe(3)); this induces a lengthening of the Fe(1)–Fe(2) bond [*e.g.* 9,11,12,14].

This steric explanation was first suggested by Doedens [12] for $[Fe_3(CO)_9(\mu_3\text{-NMe})_2]$ but never tested in a systematic way. However, the asymmetry is also present in types (b) and (c), even if it is smaller. A good example is $[Fe_3(CO)_9(\mu_3\text{-S})(\mu_3\text{-PPh})]$ [18] where, in the asymmetric crystal unit, a molecule of both type (b) and of type (c) are present (Table 2).

Considering the packing of the molecules in the lattices, an increased closed packing is observed in the sequence SSe, STe, SeTe, related strictly to the increase of the chalcogen atom dimensions. In fact in the SSe complex, no intermolecular contact is detected; in the STe complex, the Te atom contacts an adjacent CO group (Te ··· O_{CO} 3.49 Å) (Fig. 4); in the SeTe complex the Te has an increased number of contacts with the neighbouring COs (Te ··· O_{CO} 3.46 and 3.63 Å) and also contacts Se atoms (Te ··· Se 4.00 Å), according to the pattern of Fig. 5.

3. Experimental details

The three complexes were prepared according to ref. 1 and crystallized at −12°C from petroleum ether solutions. Crystal data are collected in Table 3. The intensity data were collected at room temperature. The structures, all isomorphous with $[Fe_3(CO)_9X_2]$, were

TABLE 3. Crystal data for $[Fe_3(CO)_9XY]$ (X, Y = S, Se, or Te)

Empirical Formula	$C_9Fe_3O_9SSe$	$C_9Fe_3O_9STe$	$C_9Fe_3O_9SeTe$
Color; habit	Dark-red, prismatic	Dark-red, prismatic	Dark-red, needle
Crystal size (mm)	0.2 × 0.1 × 0.1	0.3 × 0.3 × 0.4	0.7 × 0.2 × 0.1
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions			
a (Å)	6.8346(10)	6.9956(8)	6.9640(12)
b (Å)	9.186(2)	9.3675(14)	9.360(2)
c (Å)	13.121(3)	13.0584(16)	13.189(2)
α (°)	93.79(3)	93.227(11)	94.090(16)
β (°)	94.21(3)	94.031(10)	94.540(15)
γ (°)	110.89(3)	111.138(10)	110.670(16)
Volume ($Å^3$)	763.8(3)	793.1(2)	797.3(3)
Z	2	2	2
Formula weight	530.7	579.3	626.2
Density (calc.) ($Mg\ m^{-3}$)	2.307	2.426	2.608
Absorption coefficient (mm^{-1})	5.130	4.683	6.588
F (000)	508	544	580

TABLE 4. Collection, solution and refinement data for $Fe_3(CO)_9XY$ (X, Y = S, Se, Te)

	XY = SSe	XY = STe	XY = SeTe
Diffractometer used	Siemens P4	Siemens P4	Siemens R3m/V
Radiation	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)
Monochromator	Highly oriented graphite crystal	Highly oriented graphite crystal	Highly oriented graphite crystal
2θ range (°)	2.0–55.0	2.0–55.0	2.0–50.0
Scan type	$2\theta-\theta$	$2\theta-\theta$	ω
Scan speed (°/min in ω)	Variable; 4.19–29.30	Variable; 4.00–29.00	Variable; 1.50–15.00
Scan range (ω) (°)	2.40 plus $K\alpha$-separation	2.40 plus $K\alpha$-separation	1.30
Background measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 37.5% of total scan time	Stationary crystal and stationary counter at beginning and end of scan, each for 35.0% of total scan time	Stationary crystal and stationary counter at beginning and end of scan, each for 30.0% of total scan time
Standard reflections	2 measured every 50 reflections	2 measured every 50 reflections	1 measured every 50 reflections
Index ranges	$-8 \leq h \leq 8$, $-11 \leq k \leq 11$, $-17 \leq l \leq 17$	$-9 \leq h \leq 9$, $-12 \leq k \leq 12$, $-16 \leq l \leq 16$	$-8 \leq h \leq 8$, $-11 \leq k \leq 11$, $0 \leq l \leq 15$
Reflections collected	7031	6244	2954
Independent reflections	3533 (R_{int} = 3.29%)	3654 (R_{int} = 1.55%)	2817 (R_{int} = 2.75%)
Observed reflections	3127 ($F > 4.0\sigma(F)$)	3465 ($F > 4.0\sigma(F)$)	2569 ($F > 4.0\sigma(F)$)
Absorption correction	Semi-empirical	Semi-empirical	Semi-empirical
Min./max. transmission	0.058/0.156	0.0461/0.0916	0.435/0.996
System used	Siemens SHELXTL PLUS (PC Version)	Siemens SHELXTL PLUS (PC Version)	Siemens SHELXTL PLUS (PC Version)
Refinement method	Full-matrix least-squares	Full-matrix least-squares	Full-matrix least-squares
Quantity minimized	$\Sigma w(F_o - F_c)^2$	$\Sigma w(F_o - F_c)^2$	$\Sigma w(F_o - F_c)^2$
Extinction correction	$\chi = 0.0055(2)$, where $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$	$\chi = 0.00017(12)$, where $F^* = F[1 + 0.002\chi F^2/\sin(\theta)]^{-1/4}$	$\chi = 0.0016(2)$, where $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0001F^2$	$w^{-1} = \sigma^2(F) + 0.0000F^2$	$w^{-1} = \sigma^2(F) + 0.0010F^2$
Number of parameters refined	210	209	210
Final R indices (obs. data)	$R = 2.57\%$, $R_w = 3.22\%$	$R = 4.19\%$, $R_w = 6.29\%$	$R = 3.01\%$, $R_w = 4.40\%$
R indices (all data)	$R = 2.94\%$, $R_w = 3.74\%$	$R = 4.34\%$, $R_w = 6.30\%$	$R = 3.33\%$, $R_w = 4.56\%$
Goodness-of-fit	1.54	6.43	1.20
Largest and mean Δ/σ	0.004, 0.001	1.477, 0.013	0.011, 0.003
Data-to-parameter ratio	14.9:1	16.6:1	12.2:1
Largest difference peak (e Å^{-3})	0.46	2.43	1.42
Largest difference hole (e Å^{-3})	0.00	−0.89	0.00

solved using the approximate coordinates of the heavy atoms of known complexes and with the aid of subsequent difference Fourier maps. All the atoms were refined anisotropically.

Table 4 lists all the parameters of the data collection and of the refinement, and Table 5 lists the fractional atomic coordinates and the thermal U_{eq} parameters. During the refinement, the values of the Fe–X/Fe–Y distances and the presence of some peaks around X/Y on the Fourier difference maps suggested a disorder of the X/Y atoms with respect to the Fe_3 plane. In the SSe and SeTe complexes, the structure was refined putting the chalcogen atoms in the same position and using complemetary occupancy factors; the satellite peaks disappeared with a great improvement in the GOOF factor. The disordered model is consistent with a distribution of 0.72/0.28 and 0.60/0.40 for the SSe and SeTe complexes, respectively. For the STe compound, even if some spurious peaks were attributed to this disorder, the greater difference between the S–Fe and Te–Fe distances did not permit the previous type of refinement; furthermore, the refinement with separate atoms did not allow a good refinement and the GOOF increased.

The observed and calculated structure factors and the anisotropic thermal parameters are available from the author.

Acknowledgement

Thanks are due to Professors R. Rossetti and P.L. Stanghellini for supplying the samples of the compounds.

TABLE 5. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$)

	x	y	z	U_{eq} [a]
[$Fe_3(CO)_9SSe$]				
Fe(1)	4182(1)	2659(1)	1601(1)	38(1)
Fe(2)	2870(1)	1957(1)	3391(1)	38(1)
Fe(3)	1335(1)	−881(1)	2433(1)	39(1)
S	777(1)	1247(1)	1854(1)	42(1)
Se	4885(1)	758(1)	2509(1)	39(1)
C(11)	4058(4)	1810(3)	330(2)	49(1)
O(11)	3915(4)	1238(3)	−483(2)	76(1)
C(12)	6962(4)	3840(3)	1762(2)	50(1)
O(12)	8703(3)	4560(3)	1852(2)	76(1)
C(13)	3481(4)	4317(3)	1287(3)	55(1)
O(13)	3094(4)	5356(3)	1074(3)	91(1)
C(21)	5080(4)	3723(3)	3826(2)	52(1)
O(21)	6451(3)	4831(3)	4135(2)	74(1)
C(22)	971(4)	2750(3)	3819(2)	52(1)
O(22)	−217(3)	3237(3)	4088(2)	81(1)
C(23)	2806(5)	882(3)	4481(2)	57(1)
O(23)	2780(5)	239(3)	5201(2)	87(1)
C(31)	−1399(4)	−1750(3)	2668(2)	52(1)
O(31)	−3112(3)	−2326(3)	2779(2)	80(1)
C(32)	2065(4)	−2242(3)	3185(2)	52(1)
O(32)	2513(4)	−3090(3)	3650(2)	78(1)
C(33)	1070(4)	−1897(3)	1195(2)	47(1)
O(33)	872(4)	−2494(3)	392(2)	71(1)
[$Fe_3(CO)_9STe$]				
Fe(1)	4130(1)	2767(1)	1571(1)	38(1)
Fe(2)	2929(1)	1962(1)	3406(1)	36(1)
Fe(3)	1419(1)	−869(1)	2444(1)	38(1)
S	893(2)	1232(1)	1874(1)	28(1)
Te	5176(1)	807(1)	−2458(1)	42(1)
C(11)	4000(10)	2027(8)	282(5)	53(2)
O(11)	3817(10)	1514(8)	−551(4)	88(3)
C(12)	6820(10)	4048(7)	1718(5)	51(2)
O(12)	8460(8)	4788(7)	1799(5)	83(3)
C(13)	3250(11)	4334(8)	1361(6)	59(3)
O(13)	2751(11)	5331(7)	1181(6)	99(3)
C(21)	5103(10)	3632(7)	3877(5)	51(2)
O(21)	6481(8)	4712(6)	4193(4)	77(2)
C(22)	1098(10)	2779(8)	3824(5)	50(2)
O(22)	−44(9)	3265(7)	4075(5)	81(3)
C(23)	2742(12)	845(8)	4475(5)	57(3)
O(23)	2689(12)	172(8)	5187(4)	95(3)
C(31)	−1243(10)	−1708(7)	2708(5)	50(2)
O(31)	−2921(8)	−2301(7)	2864(5)	78(2)
C(32)	2120(10)	−2220(8)	3190(5)	54(2)
O(32)	2560(10)	−3056(7)	3649(5)	86(3)
C(33)	1160(10)	−1813(7)	1199(5)	49(2)
O(33)	997(10)	−2392(6)	380(4)	75(3)
[$Fe_3(CO)_9SeTe$]				
Fe(1)	4230(1)	2709(1)	1609(1)	36(1)
Fe(2)	2868(1)	1912(1)	3410(1)	35(1)
Fe(3)	1336(1)	−977(1)	2456(1)	36(1)
Te	4997(1)	699(1)	2492(1)	39(1)
Se	657(1)	1177(1)	1784(1)	40(1)
C(11)	4141(8)	1965(6)	325(4)	52(2)
O(11)	4047(7)	1475(6)	−495(3)	85(2)
C(12)	6944(8)	3870(5)	1810(4)	49(2)
O(12)	8639(6)	4594(5)	1915(4)	76(2)
C(13)	3499(8)	4334(6)	1370(4)	55(2)
O(13)	3090(8)	5377(5)	1205(5)	96(2)
C(21)	5043(8)	3602(6)	3858(4)	50(2)
O(21)	6410(6)	4680(5)	4188(3)	75(2)
C(22)	1032(7)	2722(6)	3829(4)	51(2)
O(22)	−87(7)	3232(6)	4117(4)	80(2)
C(23)	2783(8)	824(6)	4473(3)	52(2)
O(23)	2721(8)	189(6)	5181(3)	85(2)
C(31)	−1316(8)	−1812(5)	2732(4)	50(2)
O(31)	−2971(6)	−2397(5)	2878(4)	82(2)
C(32)	2114(8)	−2254(5)	3211(4)	50(2)
O(32)	2603(7)	−3095(5)	3668(3)	77(2)
C(33)	1025(7)	−2008(5)	1229(4)	47(2)
O(33)	806(7)	−2639(5)	437(3)	73(2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

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