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## The Crystal and Molecular Structure of Ethylenediammonium Bis- $\{cis\text{-[ethylenediaminedisulphitoaurate(III)]}\}^*$

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$(C_2H_{10}N_2)^{2+}[Au(SO_3)_2en]_2^-$  is triclinic with  $a=7.975$  (1),  $b=7.872$  (1),  $c=9.198$  (1) Å;  $\alpha=93.88$  (2),  $\beta=94.90$  (2),  $\gamma=100.07$  (1)°;  $Z=1$ ; space group  $P\bar{1}$ . The structure was solved by Patterson and Fourier techniques and refined to a final  $R$  of 0.047. The aurate ion is essentially square-planar; the ligands are two N atoms from an ethylenediamine molecule and two S atoms from the sulphito groups. The geometry of the  $SO_3$  groups is that of coordinated groups through the sulphur atoms to the metal, rather than the geometry of sulphite ions. All the H atoms of ethylenediamine, as well as those attached to the carbon atoms of ethylenediammonium, were located from a difference synthesis. Only one H atom of the  $NH_3^+$  group was clearly located; this was sufficient to define the orientation of the group and to obtain a complete view of the three-dimensional network of hydrogen bonds in the crystal.

### Introduction

The gold(III) complexes  $X^{n+}[Au(SO_3)_2en]_n^-$  ( $n=1$ ,  $X=Na, K, NH_4$ ;  $n=2$ ,  $X=C_2H_{10}N_2$ ) display interesting electrochemical properties and have gained technological importance in electrodeposition of gold and its alloys (Zuntini, Aliprandini, Gioria, Meyer & Losi, 1974). The present X-ray structure analysis was prompted by the general lack of crystallographic information on gold(III) sulphito complexes and by the need to disclose the stereochemical arrangement in the coordination sphere of gold to relate function to structure. The oxidation state of gold was ascertained by photoelectron spectroscopy (Jørgensen, 1973).

### Experimental

The monocationic complexes are unstable in the solid state and form exceedingly thin flakes which are not

suitable for X-ray investigation. On the other hand the ethylenediammonium derivative proved to be quite adequate. On cooling, large colourless prisms, elongated along  $a$ , were obtained from moderately warm aqueous solutions of any of the monocationic complexes with an excess of ethylenediamine. The crystals decompose slowly with formation of metallic gold, but remain stable long enough for data collection when sealed under argon in Lindemann capillaries. The lattice parameters and the intensities were measured at room temperature on an automatic four-circle Philips PW1100 diffractometer with graphite-monochromatized  $Mo K\alpha$  radiation ( $\lambda=0.71069$  Å).

### Crystal data

$(C_2H_{10}N_2)[Au(SO_3)_2(C_2H_8N_2)]_2$ ;  $M=896.31$ . Triclinic; space group  $P\bar{1}$ ,  $a=7.975$  (1),  $b=7.872$  (1),  $c=9.198$  (1) Å,  $\alpha=93.88$  (2),  $\beta=94.90$  (2),  $\gamma=100.07$  (1)°;  $V=566.7$  Å<sup>3</sup>;  $Z=1$ ;  $D_m=2.737$ ;  $D_x=2.627$  g cm<sup>-3</sup>;  $\mu=143.24$  cm<sup>-1</sup>.

With a crystal of dimensions  $0.19 \times 0.16 \times 0.16$  mm, 3609 independent reflexions were scanned in the  $\theta$ - $2\theta$  mode (scan width  $1.0^\circ$  in  $2\theta$ ; scan speed  $0.04$  s<sup>-1</sup>) with

\* A summary of this work was presented at the meeting of the Swiss Crystallographical Society, October 1973, Treviso/Lugano (Dunand & Gerdil, 1974).

$\sin \theta/\lambda < 1.1$ . The background was measured on each side of the peaks with a counting time of half the reflexion scan time. Three monitor reflexions, measured at average intervals of 25 reflexions, were used to correct for intensity variations. The usual corrections were applied and 3470 reflexions, with  $|F_o| > 2\sigma(F_o)$ , were obtained. It later proved useful (see below) to remeasure 600 low-order reflexions ( $\sin \theta/\lambda < 0.44$ ; scan speed  $0.02^\circ \text{ s}^{-1}$ ) with a smaller crystal of  $0.11 \times 0.09 \times 0.08$  mm. 245 structure amplitudes with  $\sin \theta/\lambda < 0.30$  were substituted for the former ones in the original set, and the remaining intensities were used for cross-correlation. The new data set was used in the final stages of refinement.

### Determination and refinement of the structure

Scattering factors for neutral atoms were used. The gold scattering factor was corrected for anomalous dispersion with constant average values  $\Delta f' = -2.4$  and  $\Delta f'' = 9.6$  for the real and imaginary components.

The relative positions of the gold atoms were obtained from a sharpened Patterson function. The structure was first analysed in space group  $P1$ . A Fourier synthesis phased by the gold atoms, one placed at  $(0, 0, 0)$ , revealed the positions of two  $\text{SO}_3$  groups and two N atoms around each metal atom. A subsequent electron density calculation revealed the entire structure except for the H atoms. Three cycles of full-matrix refinement with anisotropic thermal parameters reduced  $R$  to 0.050. At this point, a plot showed an undue increase of  $|\Delta F|/|F_o|$  with decreasing reflexion angle ( $\sin \theta/\lambda < 0.25$ ), a likely result of the neglect of absorption corrections. Low-angle reflexions were again recorded with a smaller crystal and the new structure amplitudes used in the completion of the refinement. Little improvement occurred in  $|\Delta F|/|F_o|$  which decreased by about 15% in the range concerned. At this stage, the mutual orientation of the two, apparently enantiomeric,  $[\text{Au}(\text{SO}_3)_2\text{en}]^-$  groups was suggestive of the presence of an intervening symmetry

centre between them. This being the case, this centre would also have to be a symmetry element of the crystal lattice implying space group  $P\bar{1}$ . The centre of gravity of the grouping  $[\text{Au}(\text{SO}_3)_2\text{en}]_2^-$  was found at  $[0.2367(8), -0.0346(6), 0.0088(6)]$ . This position was not significantly different from the average position  $[0.2355(65), -0.0352(68), 0.0081(72)]$  of the centre of a line joining any two symmetry equivalent atoms in the postulated centrosymmetric dianion. A further consequence of a centrosymmetric space group was that the unique ethylenediammonium ion should be planar and in a special position. This was the case: the centres of gravity of the anionic and cationic components being separated by translations close to  $\frac{1}{2}$  along the cell edges. Space group  $P\bar{1}$  was therefore considered to be consistent with our data within limits of error. In the centrosymmetric refinement the origin was fixed at the centre of the ethylenediammonium ion. Only small shifts occurred in the parameters. From a difference map all the H atoms of the ethylenediamine molecule, as well as those attached to the C atoms of ethylenediammonium, were located, whereas only one peak had a high enough density to be assigned as an H atom in the  $-\text{NH}_3^+$  group. This was sufficient to define the orientation of the group and to calculate the positions of the two remaining H atoms, assuming tetrahedral symmetry. Hydrogen atoms were included but not refined. The condition for inclusion of a reflexion was:  $|F_o| > 2\sigma(F_o)$ ; if  $|F_c| > |F_o|$  when  $2\sigma(F_o) \leq |F_o| < 3\sigma(F_o)$ . The final  $R$ , based on 3470 reflexions, was 0.047 with the weighting scheme:  $\omega = 0.043 F_o$  for  $|F_o| < 14.9$ ,  $\omega = 1.0$  for  $F_o$  in the range  $14.9-64.8$ , and  $\omega = 32.5 F_o^{-1}$  for  $|F_o| > 64.8$ . The final values of the positional and vibrational parameters are listed in Tables 1 and 2.\*

\* A table of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30662 (22 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Final positional and thermal parameters (both  $\times 10^4$ ) with standard deviations in parentheses

Thermal parameters are given in the form:  $\exp [-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$ .

	$x$	$y$	$z$	$b_{11}$	$b_{22}$	$b_{33}$	$b_{12}$	$b_{13}$	$b_{23}$
Au	2689 (0)	5416 (0)	4870 (0)	36 (1)	37 (1)	33 (0)	12 (1)	6 (0)	4 (0)
N(1)	2632 (10)	5599 (10)	7174 (7)	109 (14)	63 (12)	42 (7)	13 (16)	9 (13)	14 (12)
C(1)	2934 (13)	7471 (13)	7708 (9)	88 (17)	92 (16)	55 (8)	53 (21)	10 (16)	-17 (15)
C(2)	4299 (13)	8484 (12)	6904 (10)	87 (16)	75 (15)	63 (9)	18 (20)	-19 (16)	-15 (15)
N(2)	3790 (10)	8094 (10)	5301 (8)	87 (13)	62 (12)	57 (7)	20 (16)	12 (13)	-0 (12)
S(1)	2618 (3)	5544 (3)	2374 (2)	56 (3)	67 (3)	44 (2)	35 (4)	10 (3)	12 (3)
O(1)	3746 (10)	4446 (10)	1764 (7)	103 (13)	127 (14)	63 (7)	97 (19)	34 (13)	-5 (14)
O(2)	811 (9)	5044 (10)	1777 (7)	64 (12)	140 (14)	59 (7)	25 (18)	-5 (12)	24 (14)
O(3)	3263 (10)	7389 (10)	2172 (8)	115 (13)	80 (12)	77 (8)	24 (17)	30 (14)	59 (14)
S(2)	1566 (3)	2498 (3)	4773 (2)	53 (3)	52 (3)	48 (2)	11 (4)	6 (3)	10 (3)
O(4)	2804 (9)	1813 (10)	5735 (9)	90 (12)	78 (13)	108 (9)	70 (17)	-21 (15)	49 (15)
O(5)	-59 (9)	2458 (10)	5413 (9)	62 (12)	99 (13)	107 (9)	14 (17)	57 (15)	35 (16)
O(6)	1351 (12)	1699 (10)	3291 (8)	174 (16)	88 (13)	58 (7)	-48 (20)	32 (15)	-33 (13)
N(3)	148 (11)	1356 (11)	-1598 (8)	113 (15)	79 (14)	54 (7)	47 (19)	11 (14)	24 (14)
C(3)	-361 (12)	798 (13)	-183 (9)	96 (17)	85 (16)	57 (8)	87 (22)	29 (15)	21 (15)

Table 2. *Positional parameters of the hydrogen atoms*  
( $\times 10^4$ )

*B* is equal to the isotropic thermal parameter of the carbon atom to which H is bonded.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ( $\text{\AA}^2$ )
H(1)	3457	4890	7716	1.61
H(2)	1391	5179	7345	1.61
H(3)	3135	7543	8767	1.77
H(4)	1786	7773	7426	1.77
H(5)	5557	8005	7121	1.95
H(6)	4472	9701	7290	1.95
H(7)	4588	8191	4724	1.60
H(8)	2718	8637	4981	1.60
H(9)	1451	1811	-1512	1.80
H(10)	-420	2215	-1848	1.80
H(11)	-165	325	-2388	1.80
H(12)	-1648	397	-278	1.40
H(13)	56	1781	573	1.40

### Discussion of the results

The molecule is best viewed as consisting of two square planar aurate ions related through a centre of inversion coincident with the centre of an intervening planar ethylenediammonium ion. A perspective drawing of the conformation of the anionic and cationic components is shown in Fig. 1, with atom numbering. Fig. 2 is a stereoscopic view of the contents of the cell. Bond lengths and angles are given in Table 3. Bond distances involving H atoms (not listed) are determined within reasonable limits of error and have mean value 1.00 (7)  $\text{\AA}$ , whereas bond angles have large mean deviations of about 5°. This is a consequence of the elongated shape, perpendicular to the bond, observed for most of the peaks assigned to H atoms.

The gold atom is surrounded by two nitrogen atoms of one ethylenediamine molecule, and two sulphur atoms, in an essentially square-planar arrangement. The distances from the least-squares plane ( $\text{\AA}$ , in parentheses) are: Au (0.028), N(1) (-0.076), N(2) (0.061), S(1) (-0.062), S(2) (0.050). The sulphito groups are crystallographically non-equivalent and both have very nearly  $C_s$  symmetry, with the mirror plane almost coincident with the best plane through Au and its ligands. The basal planes of the  $\text{SO}_3$  pyramids, defined by O(1), O(2), O(3) and O(4), O(5), O(6), make di-

hedral angles 88.3° and 90.4°, respectively, with the plane through Au, S(1) and S(2). The projection of the  $\text{SO}_3$  group on a plane perpendicular to the S(1)···S(2) line shows a staggered conformation which allows the S atoms to come closer together with proper orientation of the lone electron pairs towards the central metal atom. Owing to intramolecular repulsion by the intervening O(6), the distance 2.468 (8)  $\text{\AA}$  between O(1) and O(2) is significantly larger than the mean value 2.425 (2)  $\text{\AA}$  calculated for O···O separation in both  $\text{SO}_3$  groups. As pointed out by Kierkegaard, Larsson & Nyberg (1972), the O···O separations in the  $\text{SO}_3$  pyramids of several metal sulphites are found to lie within a narrow range: the unweighted mean value calculated over 27 distances is 2.415 (21)  $\text{\AA}$ . The over-

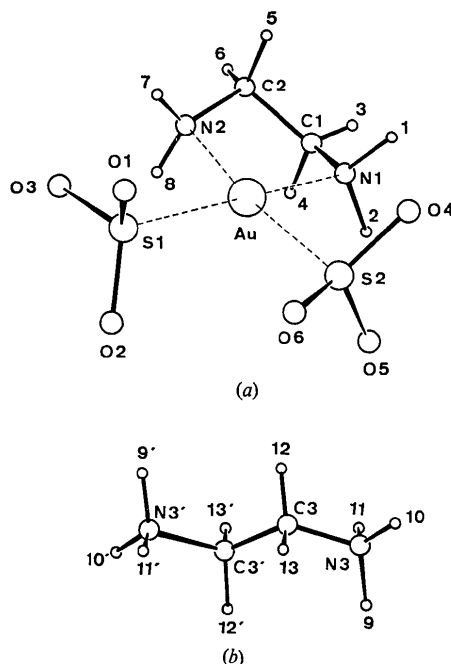


Fig. 1. Perspective drawing and atom-numbering of the aurate ion (a) and of the ethylenediammonium ion (b).

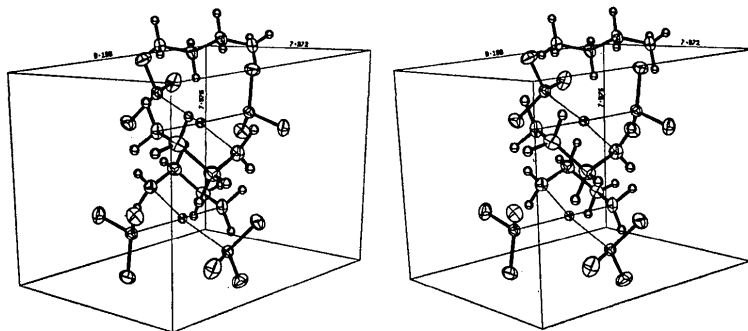


Fig. 2. Stereoscopic view of the contents of one unit cell. The origin, upper rear corner, is fixed at the centre of inversion of one ethylenediammonium ion. The asymmetric unit consists of one half formula unit. The ellipsoids are plotted at 50% probability level and the H atoms are given an artificial radius of 0.1  $\text{\AA}$ .

Table 3. *Intramolecular parameters with their estimated standard deviations*

Bond distances (Å)			
Au—N(1)	2.119 (7)	S(2)—O(5)	1.465 (6)
Au—N(2)	2.133 (7)	S(2)—O(6)	1.445 (7)
Au—S(1)	2.301 (2)	N(1)—C(1)	1.493 (11)
Au—S(2)	2.308 (2)	N(2)—C(2)	1.492 (11)
S(1)—O(1)	1.470 (7)	C(1)—C(2)	1.511 (12)
S(1)—O(2)	1.473 (6)	N(3)—C(3)	1.469 (11)
S(1)—O(3)	1.483 (7)	C(3)—C(3')	1.517 (12)
S(2)—O(4)	1.466 (7)		
Bond angles (°)			
N(1)—Au—N(2)	81.9 (3)	N(1)—C(1)—C(2)	110.1 (7)
N(2)—Au—S(1)	92.8 (2)	N(2)—C(2)—C(1)	108.0 (7)
S(1)—Au—S(2)	95.6 (2)	N(3)—C(3)—C(3')	110.5 (7)
S(2)—Au—N(1)	89.8 (2)	Au—S(1)—O(1)	110.2 (3)
O(1)—S(1)—O(2)	113.9 (4)	Au—S(1)—O(2)	106.8 (3)
O(1)—S(1)—O(3)	110.3 (4)	Au—S(1)—O(3)	104.9 (3)
O(2)—S(1)—O(3)	110.3 (4)	Au—S(2)—O(4)	103.6 (3)
O(4)—S(2)—O(5)	111.4 (5)	Au—S(2)—O(5)	103.4 (3)
O(4)—S(2)—O(6)	113.0 (4)	Au—S(2)—O(6)	111.7 (3)
O(5)—S(2)—O(6)	112.9 (4)		
Distances involving non-bonded atoms (Å)			
N(1)···N(2)	2.788 (10)	O(2)···O(6)	3.138 (10)
N(1)···S(2)	3.128 (7)	N(1)···O(4)	3.208 (10)
S(1)···N(2)	3.215 (7)	N(1)···O(5)	3.217 (10)
S(1)···S(2)	3.413 (3)	N(2)···O(3)	2.875 (10)
O(1)···O(6)	3.118 (10)		

all geometry of the sulphite groups in several crystal structure was discussed by Kierkegaard *et al.* (1972, and references therein) in terms of environmental effects and bonding character. The O—S—O angles (here-

after denoted  $\theta_{OSO}$ ) decrease regularly with increasing S—O distances (hereafter denoted  $r_{SO}$ ). A good linear correlation ( $\rho=0.9990$ ) is obtained on the basis of 12 observational pairs ( $r_{SO}$ ,  $\theta_{OSO}$ ), including averaged values (1.475 Å, 111.5°) and (1.459 Å, 112.4°) for the  $SO_3$  groups of the present compound. The regression line is given by

$$\theta_{OSO}(\text{°}) = -128.4r_{SO}(\text{Å}) + 300.1$$

and the standard error of estimate of  $\theta_{OSO}$  on  $r_{SO}$  is 0.9°. The short  $r_{SO}$ 's and the larger than tetrahedral  $\theta_{OSO}$ 's reported here definitely suggest coordination to the metal atom, rather than interionic interaction, when compared with values observed in the sulphonate compound  $K_2[CH_2(SO_3)_2]$  and in the  $SO_4^{2-}$  ion. Environmental effects are also exerted on the sulphite oxygen atoms by participation in the extensive hydrogen-bond network in the present crystal structure. The expected lengthening effect on the S—O bonds is opposed to the shortening effect arising from the participation of the sulphur lone pair in the  $Au^{III}$ —S bond. If this bond (mean value 2.305 Å) is regarded as a pure single bond, the approximate value 1.27 Å is calculated for the  $Au^{III}$  radius, taking a radius of 1.04 Å for tetrahedral sulphur. This compares well with the average value 1.31 Å estimated from the bond distances in gold(III) chloride (Clark, Templeton & MacGillavry, 1958).

Ethylenediamine is in a *gauche* conformation with a N—C—N torsional angle of 53.3° and with C—N

Table 4. *Distances and angles for possible N—H···O hydrogen-bonded contacts*

Interactions occur between a donor group in the basic part of the molecule at  $x, y, z$  and an acceptor oxygen in the related part at  $\bar{x} + t_x, \bar{y} + t_y, \bar{z} + t_z$ . The e.s.d.'s are about 0.08 Å in the H···O distances and 7° in the bond angles.

Donor	Acceptor	$t_x, t_y, t_z$	Distances (Å)		Angles (°)	
			N···O	H···O	N—H···O	H···O—S
N(1)—H(1)	O(1)	1 1 1	2.977	2.20	129	121
N(1)—H(2)	O(2)	0 1 1	2.959	1.98	161	134
N(2)—H(7)	O(4)	1 1 1	2.945	2.16	152	123
N(2)—H(8)	O(5)	0 1 1	2.941	2.14	132	142
N(3)—H(10)	O(2)	0 1 0	3.072	2.23	154	93
N(3)—H(10)	O(3)	0 1 0	3.069	2.34	137	88
N(3)—H(11)	O(6)	0 0 0	2.794	1.81	157	135

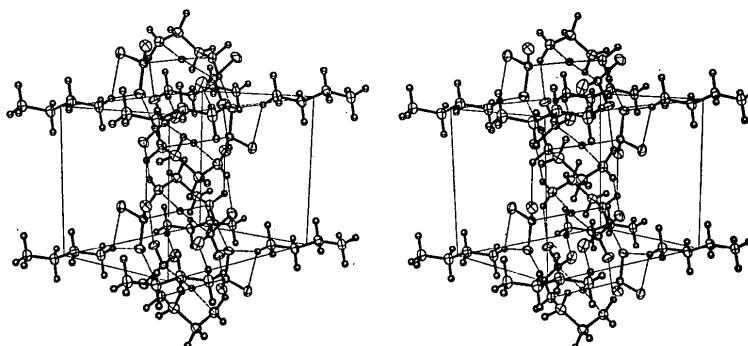


Fig. 3. Stereoscopic view of the molecular packing showing the hydrogen-bond network. For clarity, several molecular components are represented in addition to the unit-cell contents. Unit-cell contours ·····; coordinative bonds —; hydrogen-bonded contacts - - -.

bond distances longer than those in the *trans* isomer (Jamet-Delcroix, 1973), as well as the mean value 1.472 ( $\pm 5$ ) Å found in different structures (Kennard *et al.*, 1972). The nitrogen lone pair orbitals point towards Au as suggested by the roughly tetrahedral bond distribution around the N atoms and the Au–N–C bond angles, 108.3° and 109.2°, at N(1) and N(2) respectively.

The enantiomeric anions and the ethylenediammonium cations are packed in three distinct sheets stacked parallel to (100). The components of a given sheet are all identical and equivalent through the *b* and *c* displacements. The sheets containing the aurate ions are related by centres of inversion and are separated, in pairs, by interleaved ethylenediammonium ions. The planar anionic moieties are piled up along [100], their mean plane forming an angle with *a*. In this direction, the Au atoms are located at the vertices of infinite zig-zag chains and subtend an angle of 159.9°; the metal atoms are alternately separated by distances of 3.846 and 4.254 Å, indicative of no interaction.

A three-dimensional network of hydrogen bonds is mainly responsible for the cohesion of the crystal lattice, as pictured stereoscopically in Fig. 3. A list of the possible hydrogen-bonded contacts is given in Table 4. All oxygen and hydrogen atoms, except H(9), are involved in hydrogen bonding. The H(9)···O(4) distance of 2.836 Å and the N(3)···O(4) distance of 3.373 Å are slightly longer than the sum of the corresponding van der Waals radii. Apart from a slight lengthening of the N···O distances, the hydrogen

bond contraction is still operating despite the sharing of H(10) by two oxygen atoms of one sulphito group and the resulting small H···O–S angles of about 90°. In the *a* direction the sulphito groups are linked through hydrogen bonds with the amino groups of ethylenediamine, whereas bonding with H atoms of the quaternary N atoms determines the packing in the (100) planes.

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## Intermetallic CoIn<sub>2</sub>, a Representative of the CuMg<sub>2</sub> Structure Type

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CoIn<sub>2</sub> prepared at 500°C crystallizes with the CuMg<sub>2</sub> structure type, space group *Fddd*. The unit cell has edge lengths *a* = 9.402, *b* = 17.846, and *c* = 5.282 Å and contains 48 atoms. Least-squares refinement of the structural parameters furnished atomic coordinates and bond lengths that were tested against a mathematically rigorous structure model based on hard-sphere contact. The model assumes spherical packing of all atoms of only two diameters and has axial ratios *a/b* = ½ and *c/b* = ½√3 and a packing density of 0.68. The agreement with the model is good; the deviations of the observed structure from the model are attributed to preferential Co–In bonds. Bonding in the other known representatives of the CuMg<sub>2</sub> type is also investigated.

### Introduction

CoIn<sub>2</sub> was established as a stable phase composition by Schöbel & Stadelmaier (1970). They showed that the phase crystallizes peritectically at 550°C and (wrongly) reported the Bravais lattice as monoclinic.

Meanwhile the lattice was found to be orthorhombic with cell parameters suggesting the CuMg<sub>2</sub> structure type (Ekwall & Westgren, 1940; Schubert & Anderko, 1951). Unlike the related CuAl<sub>2</sub> structure type, which seems ubiquitous, the CuMg<sub>2</sub> type is rarely observed. Beside CuMg<sub>2</sub> itself, only NbSn<sub>2</sub> (Gomes de Mesquita,