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References

BURBANK, R. D. (1953). *J. Amer. Chem. Soc.* **75**, 1211.
DESREUX, V. (1935). *Bull. soc. chim. Belges.* **44**, 249.
FOURME, R. & RENAUD, M. (1966). *C. R. Acad. Sci. Paris, Ser. A*, **263*b***, 69.
HIJIKIGAWA, M., HAYAFUJI, Y., IKEDA, M., FUKUSHIMA, R., KAWAGUCHI, T. & TOMIIE, Y. (1972). To be published in *Bull. Chem. Soc. Japan.*
IWATA, Y., OYAMA, M., KAWAGUCHI, T. & WATANABÉ, T. (1972). To be published.
KITAIGORODSKII, A., KHOTSYANOVA, T. L. & STRUCHKOV, YU. T. (1951). *Dokl. Akad. Nauk SSSR.* **78**, 1161.
NITTA, I. (1926). *Sci. Pap. Inst. Phys. Chem. Res.* (*Tokyo*) **4**, 49.
SCOTT, R. A. & SCHERAGA, H. A. (1965). *J. Chem. Phys.* **42**, 2209.
TOMIIE, Y. (1961). *Kwansei Gakuin Univ. Ann. Studies* **10**, 208.
WILLIAMS, Q., COX, J. T. & GORDY, W. (1952). *J. Chem. Phys.* **20**, 1524.
WYCKOFF, L. W. G. (1964). *Crystal Structures*, vol. 2, p. 70. New York, London, Sydney: Wiley-Interscience.

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The Crystal and Molecular Structure of Chromium(III) Tris-(*O*-ethylxanthate)

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Chromium(III) tris-(*O*-ethylxanthate) crystallizes in the rhombohedral space group $R\bar{3}$, with two molecules per unit cell, $a=9{\cdot}72$ Å, $\alpha=100°48'$. The crystal structure of the chromium xanthate has been refined by the least-squares method, starting from the atomic positions determined for the isostructural cobalt(III) tris-(*O*-ethylxanthate). The final agreement index for the observed reflexions was $R_1=0{\cdot}069$. Each molecule is formed by three ethylxanthate ligands coordinated to a chromium atom through the sulphur atoms; the molecule has trigonal symmetry C_3–3. The intermolecular interactions are of the van der Waals type. Mean bond lengths are Cr–S 2·393 (3) Å, S–C 1·691 (7) Å, C–O 1·297 (11) Å. The $\cdots S_2^{(-)}C=O^{(+)}R$ form makes an important contribution to the structure of the xanthate radical.

Introduction

This work is part of the program of research carried out in our laboratory on the crystal structures of dithiocarbamates and xanthates, with the aim of gaining information on metal–sulphur bonds and on the structure of dithiocarbamate and xanthate ligands.

Recently the crystal structures of cobalt(III) tris-(*O*-ethylxanthate) (Merlino, 1969) and of iron(III) tris-(*O*-ethylxanthate) (Hoskins & Kelly, 1970; Watanabe & Yamahata, 1970) were determined. It seemed useful to investigate the crystal structure of chromium(III) tris-(*O*-ethylxanthate) in order to specify which differences arise in the structure of the xanthate ligand by coordinating it to different metal atoms.

Experimental

The morphological, optical and X-ray crystallography of chromium(III) tris-(*O*-ethylxanthate) was investigated by Franzini & Schiaffino (1962); the cell data of this compound, as reported by these authors, are:

$Cr(III)(S_2COC_2H_5)_3$, M.W.415·60;
$a_{rh}=9{\cdot}72\pm0{\cdot}01$ Å, $\alpha_{rh}=100°48'\pm10'$;
$a_{hex}=14{\cdot}98$ Å, $c_{hex}=13{\cdot}31$ Å;
$U_{rh}=862{\cdot}4$ Å^3;
$D_m=1{\cdot}59$ g.cm^{-3}, $D_c=1{\cdot}591$ g.cm^{-3},
$Z=2$;
Space group $R\bar{3}$.

Throughout the present paper the rhombohedral (obverse setting) indices and coordinates will always be used.

Three-dimensional intensity data were recorded on Buerger precession photographs with the multiple-exposure technique and integration process; zirconium-filtered Mo $K\alpha$ radiation was used.

A crystal, prepared according to the method described by Franzini & Schiaffino (1962), was ground to a nearly spherical shape with a mean diameter of 0·84 mm. ($\mu R=0{\cdot}58$ for Mo $K\alpha$ radiation).

On the photographs of six layers, with [010] as the precession axis ($k=0$ to 5), a total of 902 independent reflexions were observed. The intensities, measured with a Nonius microdensitometer, were corrected for Lorentz, polarization and absorption factors by means of a data-reduction program (Catani & Zanazzi, 1965), which makes use, for the absorption factor, of the three-constants formula proposed by Palm (1964).

Determination of the structure

The structure of chromium xanthate has been determined starting from that of cobalt xanthate; coordinates and individual isotropic temperature factors derived from the latter structure were assumed for the heavy atoms and then refined by the full-matrix least-squares program of Busing, Martin & Levy adapted for the *Crystal Structure Calculations System, X-ray 63* (Stewart, 1964). At first all the reflexions were placed on the same scale by comparing the reflexions common to the various layers; subsequently the six scale factors were included among the refined parameters. After three refinement cycles with unit weights for all the observed reflexions the reliability index R_1, defined as $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, reduced from 0·306 to 0·128. Two more refinement cycles, in which anisotropic temperature factors in the form $\exp\{-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\}$ were introduced, reduced the R_1 value to 0·090.

At this stage a three-dimensional Fourier difference synthesis was calculated. The positions of the hydrogen atoms were calculated assuming: (*a*) C–H bond lengths of 1·08 Å, (*b*) tetrahedral hybridization of the carbon atoms, (*c*) staggered conformation of the ethyl groups; the positions so obtained were found to correspond to areas of positive electron density on the Fourier difference map. In the subsequent refinement the hydrogen atoms, with an isotropic thermal parameter of 5 Å²,

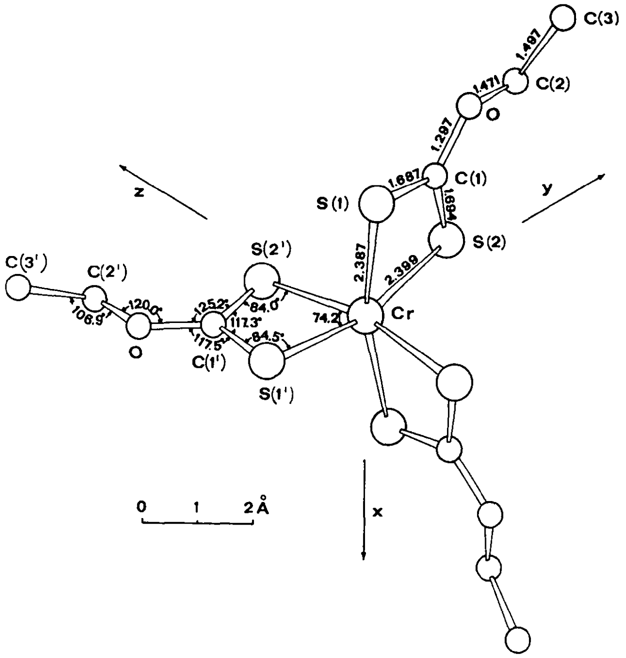


Fig. 1. The molecular structure of chromium(III) tris-(*O*-ethylxanthate).

Table 1. *Observed and calculated structure factors*

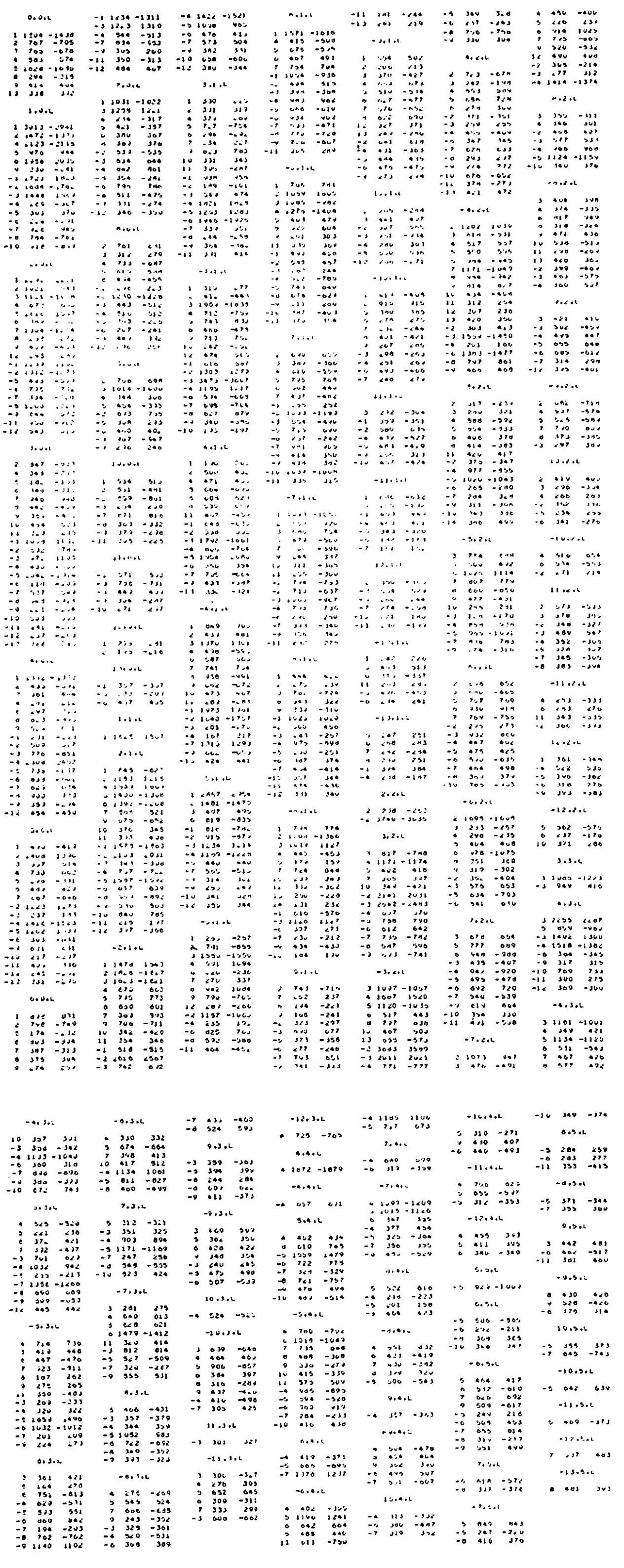


Table 2. *Positional and thermal parameters for the heavy atoms and positional parameters for the hydrogen atoms*

Standard deviations are given in parentheses. Values for the heavy atoms are multiplied by 10^4 and for the hydrogen atoms by 10^3.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr	2963 (2)	2963 (2)	2963 (2)	56 (2)	56 (2)	56 (2)	13 (2)	13 (2)	13 (2)
S(1)	2330 (2)	4809 (2)	4546 (2)	74 (2)	79 (2)	63 (2)	22 (2)	9 (2)	9 (2)
S(2)	921 (2)	3525 (2)	1566 (2)	79 (2)	85 (2)	63 (2)	25 (2)	8 (2)	7 (2)
O	223 (6)	5660 (7)	3238 (6)	89 (7)	97 (7)	82 (7)	34 (6)	12 (6)	15 (6)
C(1)	1033 (8)	4747 (8)	3099 (8)	63 (8)	59 (8)	60 (8)	− 8 (6)	5 (7)	17 (6)
C(2)	− 983 (10)	5601 (11)	2044 (10)	97 (11)	126 (13)	90 (11)	41 (10)	− 5 (9)	26 (10)
C(3)	− 1434 (13)	6995 (13)	2362 (13)	140 (15)	129 (14)	137 (15)	62 (12)	11 (12)	38 (12)

Table 2 (*cont.*)

	x	y	z
H(1)	− 67	546	103
H(2)	− 189	470	197
H(3)	− 235	702	151
H(4)	− 56	789	243
H(5)	− 178	714	337

were introduced and the following weighting scheme was applied to all the observed reflexions:

$$\sqrt{w}=(0{\cdot}01|F_o|+1)^{-1}\,.$$

Three more refinement cycles, in which the positional and thermal parameters of the hydrogen atoms were maintained constant, led to the final values of $R_1=0{\cdot}069$ and $R_2=[\sum w||F_o|-|F_c||^2/\sum w|F_o|^2]^{1/2}=0{\cdot}089$. The shifts of the parameters in the last cycle were less than one tenth of the corresponding estimated standard deviations.

The atomic scattering factors used in the structure factor calculations were taken from *International Tables for X-ray Crystallography* (1962).

The observed and calculated structure factors are compared in Table 1. The final positional and thermal parameters are given in Table 2.

Table 3. *Shortest intermolecular distances*

S(1) ··· S(1^{iii})	3·58 Å
S(1) ··· O^{ii}	3·60
S(1) ··· C(2^{ii})	3·85
S(1) ··· C(3^{ii})	3·91
S(1) ··· C(3^{v})	3·96
S(2) ··· C(2^{vi})	3·77
S(2) ··· C(3^{vi})	3·89
O ··· O^{ii}	3·95
O ··· C(2^{v})	3·54
O ··· C(3^{iv})	3·90
C(1) ··· C(3^{iv})	3·88

The atoms of the different asymmetric units are related to the symmetry equivalent atoms of the fundamental unit as follows:

i	z	x	y
ii	$-x$	$1-y$	$1-z$
iii	$1-z$	$1-x$	$1-y$
iv	$1-y$	$1-z$	$-x$
v	z	$1+x$	y
vi	$-x$	$1-y$	$-z$

Description and discussion of the structure

The structure consists of enantiomorphous molecules $Cr(S_2COC_2H_5)_3$ (Fig. 1); their crystal packing is governed by normal van der Waals interactions, as in the related compounds of Co(III) and Fe(III).

The interatomic distances and bond angles were calculated by means of the program *BONDLA* incorporated in the *Crystal Structure Calculations System*, *X-ray* 63 (Stewart, 1964). In Table 3 we report the closest intermolecular distances (less than 4·0 Å).

Intramolecular distances and bond angles are reported in Table 4 and in Fig. 1.

Table 4. *Bond distances and angles with their standard deviations*

Distances

		Mean	Calculated
Cr—S(1)	2·387 (3) Å	2·393 Å	
Cr—S(2)	2·399 (3)		
S(1) -C(1)	1·687 (7)	1·691	1·685 Å
S(2) -C(1)	1·694 (7)		
C(1)–O	1·297 (11)	1·297	1·295
O —C(2)	1·471 (11)		
C(2)–C(3)	1·497 (17)		

Angles

S(1) -Cr—S(2)	74° 14 (5)′
Cr—S(1) -C(1)	84° 28 (17)′
Cr—S(2) -C(1)	83° 57 (17)′
S(1) -C(1)–S(2)	117° 20 (29)′
S(1) -C(1)–O	117° 28 (31)′
S(2) -C(1)–O	125° 11 (33)′
C(1)–O —C(2)	120° 1 (38)′
O —C(2)–C(3)	106° 55 (43)′

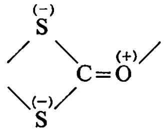
As in the crystal structures of Co(III) and Fe(III) ethylxanthates, the molecule has symmetry C_3–3, with three ethylxanthate ligands coordinated to chromium through the sulphur atoms; distances and angles in the chromium coordination sphere are given in Table 5. The six sulphur atoms form a distorted octahedron about the metal atom. All the atoms of each ligand, except the terminal carbon atom, lie approximately in a plane with the chromium atom (Table 6).

Table 5. *Distances and angles in the chromium coordination sphere*

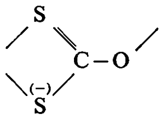
Cr—S(1)	2·387 Å	S(1)-Cr-S(2)	74° 14′
Cr—S(2)	2·399	S(1)-Cr-S(1^{i})	95 26
S(1)-S(2)	2·888	S(1)-Cr-S(2^{i})	98 11
S(1)-S(1^{i})	3·533	S(2)-Cr-S(1^{i})	163 35
S(1)-S(2^{i})	3·617	S(2)-Cr-S(2^{i})	94 19
S(2)-S(2^{i})	3·518		

The mean value of the two crystallographically independent Cr–S distances (2·393 Å) corresponds to a covalent radius for octahedrally coordinated Cr(III) of 1·35 Å, which is in a good agreement with the values obtained for Cr(III) in pnictides by Pearson (1965).

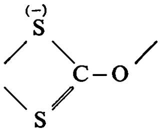
The mean values of the S–C and C–O bond lengths are 1·691 and 1·297 Å respectively (Table 4); the bond distances calculated in terms of the valence-bond theory agree well with these values, assuming the following contributions of the resonance structures:



(I) 30%



(II) 35%



(III) 35%

Bond-order/bond-length curves were derived with the use of the Pauling relation:

$$r_x = r_1 - (r_1 - r_2)\frac{3x}{2x+1}\,.$$

The values assumed were for the S–C bond $r_1 = 1{\cdot}812$ Å and $r_2 = 1{\cdot}607$ Å (Pauling, 1960); for the C–O bond $r_1 = 1{\cdot}437$ Å and $r_2 = 1{\cdot}185$ Å (Cox & Jeffrey, 1951).

It seems useful to compare the structures of cobalt, iron and chromium ethylxanthates. In Table 7 we report in the first column the electronic configuration of the metal, in the four following columns the metal-to-sulphur, sulphur-to-carbon, carbon-to-oxygen and oxygen-to-carbon bond lengths, and in the last columns the contributions of the resonance structure (I), as determined from the S–C and C–O bond lengths. The relevant feature of the Table is the decrease of the contribution of the resonance structure (I) in the sequence chromium, iron, cobalt xanthate, with a consequent shortening of S–C bond distances and lengthening of C–O bond distance. The explanation for this can be found in the increase of metal *d*-electron delocalization in the sequence Cr(III), Fe(III), Co(III); the greater the *d*-electron delocalization, the smaller the contribution of the resonance form (I). The position of Cr(III), Fe(III) and Co(III) in the nephelauxetic series (Figgis, 1966) is in harmony with our explanation.

Another point of interest of the structure is the value of 1·471 (11) Å found for the O–C bond distance, *i.e.* for the bond between the oxygen atom and the first carbon atom of the ethyl group; the deviation from the value of 1·426 Å found in paraffinic alcohols for oxygen to carbon single-bond distance is highly significant (*Tables of Interatomic Distances and Configuration in Molecules and Ions*, 1958, 1965). Such a lengthening is observed also in Fe(III) *O*-ethylxanthate (1·476 (10) Å), while in Co(III) *O*-ethylxanthate it is not significant (1·431(17) Å). The lengthening of the same bond distance has been found also in the crystal structure of sodium xanthate dihydrate (Mazzi, Tazzoli & Ungaretti, 1969) where one of the two independent ethylxanthate ligands has bond distances C–O of 1·336 (8) Å and O–C of 1·480 (13) Å, and the other has bond distances C–O of 1·321 (11) Å and O–C of 1·474 (11) Å. It appears from recent X-ray analyses of good accuracy that whenever in the ethylxanthate group the resonance form $S_2^{(-)}C{=}O^{(+)}R$ gives a substantial contribution, there is a significant lengthening of the bond between the oxygen atom and the carbon atom of the ethyl group. This structural feature can be explained (Merlino, 1972) in terms of a smaller ionic contribution to the bond in question, with a consequent lengthening of the bond over the values normally found in alcohols and ethers.

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Table 6. *Mean-plane parameters and deviations of atoms from the plane*

The equation of the plane is in the form $Ax+By+Cz=D$, where x, y and z are fractional coordinates, calculated after Schomaker, Waser, Marsh & Bergman (1959).

A	B	C	D	Atoms defining the plane
5·5587	6·2957	−5·4003	1·8949	Cr, S(1), S(2), C(1), O, C(2)

	Deviation		Deviation
Cr	−0·017 Å	C(1)	0·006 Å
S(1)	0·027	O	−0·044
S(2)	0·009	C(2)	0·019
		C(3)	−0·436

Table 7. *Comparison of some bond lengths with the electronic configuration of the metal and the contribution of the resonance structure* (I) *in* Cr(III), Fe(III) *and* Co(III) *ethylxanthates*

M	Electronic configuration	M–S	S–C	C–O	O–C	%(I)
Cr(III)	$(t_{2g})^3$	2·393 Å	1·691 Å	1·297 Å	1·471 Å	30
Fe(III)	$(t_{2g})^5$	2·312	1·685	1·328	1·476	22
Co(III)	$(t_{2g})^6$	2·277	1·673	1·359	1·431	13

References

CATANI, A. & ZANAZZI, P. F. (1965). *Ric. Sci.* **35** (II-*A*), 524.

COX, E. G. & JEFFREY, G. A. (1951). *Proc. Roy. Soc.* A**207**, 110.

FIGGIS, B. N. (1966). *Introduction to Ligand Fields*. New York: Interscience.

FRANZINI, M. & SCHIAFFINO, L. (1962). *Mem. Soc. tosc. Sci. nat.* **69**, 342.

HOSKINS, B. I. & KELLY, B. P. (1970). *Chem. Commun.* p. 45.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

MAZZI, F., TAZZOLI, V. & UNGARETTI, L. (1969). *Mem. Accad. Lincei*, **47**, 69.

MERLINO, S. (1969). *Acta Cryst.* B**25**, 2270.

MERLINO, S. (1972). In the press.

PALM, J. H. (1964). *Acta Cryst.* **17**, 1326.

PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.

PEARSON, W. B. (1965). *Z. Kristallogr.* **121**, 449.

SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). *Acta Cryst.* **12**, 600.

STEWART, J. M. (1964). *Crystal Structure Calculations System, X-Ray* 63. Tech. Rep. TR-64-6, Computer Science Center, Univ. of Maryland and Research Computer Laboratory, Univ. of Washington.

Tables of Interatomic Distances and Configuration in Molecules and Ions (1958). Special Publication No. 11. London: The Chemical Society.

Tables of Interatomic Distances and Configuration in Molecules and Ions (1965). Special Publication No. 18. London: The Chemical Society.

WATANABE, Y. & YAMAHATA, K. (1970). *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, **64**, 71.

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The Relation between Electron Concentration and Stacking Variants in the Alloy Systems Mg-Cu-Ni, Mg-Cu-Zn and Mg-Ni-Zn

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In the pseudo-binary systems $MgNi_2$–$MgZn_2$ four new stacking variants were found in the mixed region of C_{36} and C_{15} and of C_{15} and C_{14} in the phase diagram given by Lieser, K. H. & Witte, H. (*Z. Metallk.* (1952) **43**, 396). These four stacking variants are isomorphous with the ones found in the systems $MgCu_2$–$MgNi_2$ and $MgCu_2$–$MgZn_2$. Homogeneity ranges of the various stacking variants among above three systems were shown as a function of electron concentration. A remarkable correspondence was found in the relation between electron concentration and crystal structure. The following structures are given in order of increasing e/a: 4-layer, 6-layer, 3-layer, 4-layer, 10-layer, 9-layer, 8-layer and 2-layer type structure. The relation between the electron concentration and the stabilization of stacking variants is evident in these Mg-base ternary alloy systems.

Among several factors governing the crystal structure of alloy phases, the electron concentration is important for the stabilization of long period anti-phase domains (Sato & Toth, 1961, 1962) and of long period stacking order in several alloy systems (Sato, Toth, Shirane & Cox, 1966; Sato, Toth & Honjo, 1967; Sato & Toth, 1968; Pearson, 1970). The origin of the stabilization of the structure has been understood as being due to the creation of Brillouin zone boundaries at the Fermi surface. Stacking variants of the Friauf–Laves phases seem to be another example of structures resulting from this phenomenon.

Laves & Witte (1936) and Lieser & Witte (1952) reported a relationship between electron concentration and the crystal structure of Mg-base ternary Friauf–Laves phases. They discussed structural changes of Friauf–Laves phases as a function of e/a (the electron-atom ratio). For example, when Cu atoms in $MgCu_2$ are replaced by other metal of different valency, the cubic C_{15}($MgCu_2$) type structure is changed to the hexagonal C_{14}($MgZu_2$) type or C_{36}($MgNi_2$) type structures depending upon the electron concentration. Although they discussed only three fundamental structures of C_{14}, C_{15} and C_{36}, Komura, Mitarai, Nakatani, Iba & Shimizu (1970) reported similar relationships including three new stacking variants in addition to C_{14}, C_{15} and C_{36} for the systems of Mg–Zn–Cu and Mg–Zn–Ag. These new structures are called 8-, 9- and 10-layer types on the basis of the layer stacking. Komura, Nakaue & Mitarai (1972) found another new stacking variant of the 6-layer type in the system Mg–Cu–Ni. We undertook a reinvestigation of the work of Lieser & Witte (1952) for the three ternary systems Mg–Cu–Zn, Mg–Ni–Zn and Mg–Cu–Ni in order to see the dependence of the structural change on the electron concentration in more detail, and also to study the possibility of finding new stacking variants in the system of Mg–Ni–Zn as in the case of Mg–Cu–Zn and Mg–Cu–Ni.

The structures of Friauf–Laves phases and their