

(triisobutylphosphate)₂ which consistently show longer M—O distances with the acyl O atom, with average differences of 0.04 (1) and 0.13 (4) Å, respectively (Ryan & Jarvinen, 1987; Karaseva, Karasev, Udovenko & Sigula, 1983). The Th atom is 0.12 Å above the O—C—C—O plane of the BMPP anion, corresponding to a dihedral angle about the O(4)—O(5) vector of 3°. The largest deviations from the O—C—C—O plane are C(1) 0.027 and C(8) -0.028 Å. The acyl group is bent slightly (7°) out of the plane of the pyrazolone ring. The dihedral angle between the two O—C—C—O planes is 98.8°.

The Th atom is 0.11 Å out of the plane of the nitrate ligand. The Th—O distances of the nitrate anions [Th—O(1) 2.55 (1), Th—O(3) 2.68 (1) Å] are similar to the Th—O distances reported for a variety of thorium complexes containing nitrate ligands reviewed by Casellato, Vigato & Vidali (1981).

The Th—O distance of the phosphoryl O atom [Th—O(6) 2.36 Å] is significantly shorter than the Th—O distances of either anionic ligand. The Th—O(6) distance can be compared with those observed in Th(TTA)₄(TOPO) (2.30 Å; Leipoldt, Wessels & Bok, 1975), [Th(NO₃)₃{OP(NMe₂)₃]₄]₂ [Th(NO₃)₆] (average value 2.34 Å; English, du Preez, Nassimbeni & van Vuuren, 1979), [Th(NO₃)₅(OPMe₃)₂][PPh₄] and [Th(NO₃)₃(OPMe₃)₄]₂[Th(NO₃)₆] (average values 2.34 and 2.38 Å, respectively; Alcock, Esperas, Bagnall & Hsian-Yun, 1978) [TTA = 1,1,1-trifluoro-3-(2-thenoyl)acetate, TOPO = tri-*n*-octylphosphine oxide]. The average Th-to-phosphoryl O distances in these structures are also substantially shorter than the Th—O distances of the

anionic ligands, a reflection of the strong Lewis basicity of the phosphoryl donors.

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References

- ALCOCK, N. W., ESPERAS, S., BAGNALL, K. W. & HSIAO-YUN, W. (1978). *J. Chem. Soc. Dalton Trans.* pp. 638–646.
- CASELLATO, U., VIGATO, P. A. & VIDALI, M. (1981). *Coord. Chem. Rev.* **36**, 183–265.
- CHMUTOVA, M. K., PRIBYLOVA, G. A. & MYASOEDOV, B. F. (1974). *Radiokhimiya*, **17**, 220–226; *Sov. Radiochem.* **17**, 224–226.
- CROMER, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, edited by J. A. IBERS & W. C. HAMILTON, Table 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, edited by J. A. IBERS & W. C. HAMILTON, Table 2.2A. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- ENGLISH, R. P., DU PREEZ, J. G. H., NASSIMBENI, L. R. & VAN VUUREN, C. P. J. (1979). *S. Afr. J. Chem.* **32**, 119–125.
- KARASEVA, E. T., KARASEV, V. E., UDOVENKO, A. A. & SIGULA, N. I. (1983). *Koord. Khim.* **9**, 692–698; *Sov. J. Coord. Chem.* **9**, 394–400.
- LARSON, A. C. (1967). *Acta Cryst.* **23**, 664–665.
- LEIPOLDT, J. G., WESSELS, G. F. S. & BOK, L. D. C. (1975). *J. Inorg. Nucl. Chem.* **37**, 2487–2490.
- RAMAKRISHNA, V. V. & PATIL, S. K. (1984). *Struct. Bonding (Berlin)*, **56**, 35–90.
- RYAN, R. R. & JARVINEN, G. D. (1987). *Acta Cryst.* **C43**, 1295–1298.
- ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.

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Bis[diethyl(glycylhistidinato)tin]–Methanol (1/1)

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Abstract. C₂₅H₄₄N₈O₇Sn₂, *M_r* = 806.05, monoclinic, *P*2₁, *a* = 8.711 (4), *b* = 13.009 (5), *c* = 15.020 (6) Å, β = 102.91 (3)°, *V* = 1659 (1) Å³, *Z* = 2, *D_x* = 1.61 Mg m⁻³, *F*(000) = 812, λ(Mo *K*α) = 0.71073 Å, μ = 0.82 mm⁻¹, *T* = 291 (1) K. Final *R* = 0.035 for 5441 unique observed reflexions [*F* ≥ 3.0σ(*F*)]. The title compound contains two different Et₂SnGlyHis molecules and one MeOH molecule in the asymmetric unit. In one Et₂SnGlyHis molecule the polyhedron around the Sn atom is a distorted trigonal bipyramid with two αC(Et) atoms and N_{peptide} in

the equatorial plane and N_{amino} and O_{carboxylate} in the apical positions. In the other molecule the Sn atom attains hexacoordination with N_{amino}, O_{carboxylate} and the two αC(Et) atoms in the equatorial plane, and N_{peptide} and N_{imide} in the apical positions. The two molecules are linked by a hydrogen bond between the amino group of the pentacoordinated unit and O(=C)_{carboxylate} of the hexacoordinated unit.

Introduction. A series of diorganotin derivatives of dipeptides have been found to exhibit anti-leukaemic

activity (Huber & Barbieri, 1986). In the context of structure–activity relationships X-ray structure determinations of such compounds have been undertaken. These revealed in each case an essentially identical trigonal bipyramidal polyhedron around the central tin atom (Huber, Haupt, Preut, Barbieri & Lo Giudice, 1977; Preut, Mundus, Huber & Barbieri, 1986, 1989). However, from Mössbauer and vibrational spectra, solid-state structures with hexacoordinated tin were inferred (Huber, Mundus, Barbieri & Ruisi, 1986) but no single crystals had been obtained to verify this structure. We are now successful with respect to diethyltin glycyhistidinate, which in the solid state contains two different molecules and in one of these tin is hexacoordinated.

Experimental. $\text{Et}_2\text{SnGlyHis}$ has been prepared by reacting equimolar amounts of Et_2SnO and glycyhistidine for 4 h in refluxing anhydrous methanol. After evaporating the solvent *in vacuo* anhydrous *n*-pentane was added to the residue. Single crystals were obtained after prolonged standing at room temperature. Crystal size $\sim 0.22 \times 0.30 \times 0.32$ mm, $\omega/2\theta$ scan, scan speed $1.5\text{--}14.6^\circ \text{min}^{-1}$ in θ , Nicolet $R3m/V$ diffractometer, graphite-monochromated $\text{Mo } K\alpha$; lattice parameters from least-squares fit with 34 reflexions up to $2\theta = 29.1^\circ$; six standard reflexions recorded every 2.5 h, only random deviations; 6449 reflexions measured in range $1.5 \leq \theta \leq 25.0^\circ$, max. $(\sin\theta)/\lambda = 0.595 \text{ \AA}^{-1}$, $0 \leq h \leq 11$, $-16 \leq k \leq 16$, $-18 \leq l \leq 18$, after averaging ($R_{\text{int}} = 0.021$), 5883 unique reflexions, 5441 with $F \geq 3.0\sigma(F)$, Lorentz–polarization correction and absorption correction *via* ψ scans, max./min. transmission 0.95/0.80; systematic absences ($h0l$) none, $(0k0)$ $k = 2n + 1$ conform to space group $P2_1$; structure solution with direct methods, ΔF syntheses and full-matrix least-squares refinement with anisotropic temperature factors for all non-H atoms and three common isotropic temperature factors for H atoms, which were placed in geometrically calculated positions (C–H 1.08 Å), refinement on F with 5441 reflexions and 382 refined parameters; $w = 2.27/[\sigma^2(F) + (0.001 F^2)]$, $S = 0.97$, $R = 0.035$, $wR = 0.036$, $(\Delta/\sigma)_{\text{max}} = 0.02$, no extinction correction; η -refinement (Rogers, 1981) gave a value of 0.98 (6) confirming the proposed chirality, largest peak in final ΔF map ± 1.0 (4) $e \text{ \AA}^{-3}$. Atomic scattering factors for neutral atoms and real and imaginary dispersion terms from *International Tables for X-ray Crystallography* (1974); programs: *PARST* (Nardelli, 1983), *SHELX76* (Sheldrick, 1976), *SHELXTL-Plus* (Sheldrick, 1987), *PCK83* (Williams, 1984).

Discussion. The asymmetric unit and the numbering of the atoms are shown in Fig. 1 and a stereoscopic view of the unit cell in Fig. 2. Atomic parameters

and the equivalent values of the anisotropic temperature factors for the non-H atoms are listed in Table 1,* bond lengths and angles as well as some least-squares planes and dihedral angles in Table 2. The asymmetric unit contains two $\text{Et}_2\text{SnGlyHis}$ molecules and one solvent molecule MeOH . In molecule (1), the atoms bound to Sn(1) form a distorted trigonal bipyramid with O(11) and N(12) (= N_{amino}) in the axial position and N(11) (= $\text{N}_{\text{peptide}}$), C(16) and C(18) (= two C_{ethyl}) in the equatorial plane. The axial angle O(11)—Sn(1)—N(12) of $151.9(2)^\circ$ deviates appreciably from linearity. In contrast to diphenyltin glycyglycinate (Huber, Haupt, Preut, Barbieri & Lo Giudice, 1977) the tridentate anion deviates from planarity, probably due to the accommodation of the large substituent at C(12). The Sn—C(Et) distances [mean: $2.131(8) \text{ \AA}$] are nearly

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53427 (36 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

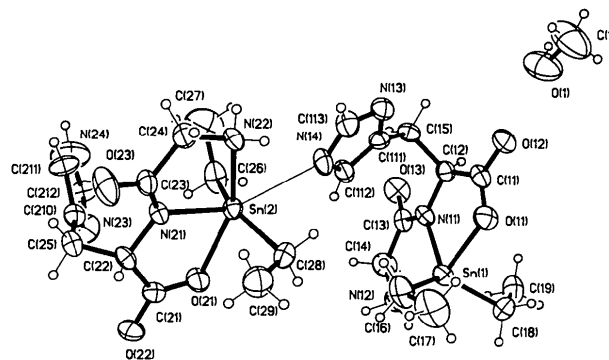


Fig. 1. General view (*SHELXTL-Plus* graphic) of the asymmetric unit showing the atom-numbering scheme.

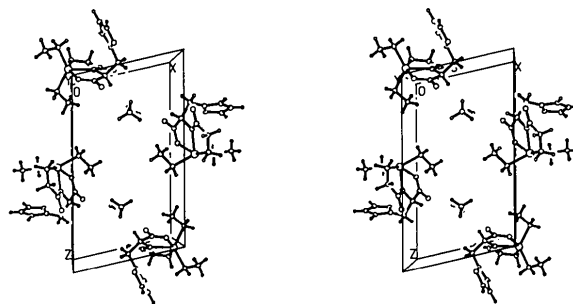


Fig. 2. Stereoscopic view (*SHELXTL-Plus* graphic) of the unit cell.

Table 1. Atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$				
	x	y	z	U_{eq}
Sn(1)	1.03118 (5)	0.0	1.06570 (2)	35
O(11)	0.9387 (5)	0.1388 (3)	0.9914 (3)	44
O(12)	0.7267 (6)	0.2210 (3)	0.9182 (3)	52
O(13)	0.5849 (6)	-0.1386 (3)	1.0105 (3)	52
N(11)	0.7861 (6)	-0.0224 (3)	1.0317 (3)	30
N(12)	1.0004 (6)	-0.1599 (4)	1.1199 (3)	42
N(13)	0.6089 (7)	0.2563 (4)	1.1314 (3)	41
N(14)	0.7422 (7)	0.1996 (4)	1.2648 (3)	42
C(11)	0.7892 (8)	0.1453 (4)	0.9622 (4)	36
C(12)	0.6871 (7)	0.0583 (5)	0.9823 (4)	34
C(13)	0.7263 (8)	-0.1140 (4)	1.0402 (4)	37
C(14)	0.8349 (9)	-0.1944 (5)	1.0898 (5)	48
C(15)	0.5610 (7)	0.0994 (5)	1.0327 (4)	35
C(16)	1.130 (1)	0.0784 (6)	1.1899 (5)	56
C(17)	1.250 (1)	0.1568 (9)	1.1831 (6)	79
C(18)	1.1435 (9)	-0.0479 (6)	0.9604 (5)	55
C(19)	1.032 (1)	-0.1154 (6)	0.8915 (5)	62
C(111)	0.6300 (6)	0.1512 (4)	1.1203 (4)	32
C(112)	0.7123 (8)	0.1192 (5)	1.2034 (4)	40
C(113)	0.6788 (8)	0.2800 (5)	1.2191 (4)	45
O(1)	0.477 (1)	0.2574 (5)	0.7789 (5)	92
C(1)	0.475 (2)	0.3533 (8)	0.7518 (9)	122
Sn(2)	-0.14218 (4)	0.16812 (4)	0.45148 (2)	30
O(21)	-0.0012 (6)	0.0408 (3)	0.5305 (3)	44
O(22)	0.1108 (5)	-0.0202 (3)	0.6678 (3)	48
O(23)	-0.1035 (8)	0.3426 (4)	0.6919 (3)	65
N(21)	-0.1132 (6)	0.2091 (3)	0.5917 (3)	29
N(22)	-0.2471 (6)	0.3280 (4)	0.4465 (3)	32
N(23)	-0.2868 (9)	-0.0525 (5)	0.6688 (5)	66
N(24)	-0.5110 (9)	0.0115 (7)	0.6566 (6)	88
C(21)	-0.0332 (7)	0.0460 (4)	0.6169 (4)	33
C(22)	-0.0230 (7)	0.1408 (4)	0.6620 (4)	30
C(23)	-0.1394 (7)	0.3040 (4)	0.6144 (4)	35
C(24)	-0.2321 (9)	0.3707 (5)	0.5384 (4)	43
C(25)	-0.1129 (7)	0.1069 (5)	0.7339 (4)	37
C(26)	-0.3423 (9)	0.0696 (6)	0.4267 (5)	50
C(27)	-0.493 (1)	0.1235 (9)	0.4214 (9)	95
C(28)	0.0692 (8)	0.2160 (6)	0.4148 (4)	46
C(29)	0.1836 (9)	0.2648 (7)	0.4950 (6)	63
C(211)	-0.2585 (8)	0.0475 (4)	0.6989 (4)	36
C(212)	-0.4076 (7)	0.0881 (4)	0.6909 (5)	42
C(213)	-0.4442 (7)	-0.0708 (4)	0.6418 (5)	40

the same as in Et₂SnCl₂ [mean: 2.150 (14) Å; Alcock & Sawyer (1977)]. In comparison to diphenyltin glycyglycinate or dicyclohexyltin glycyglycinate (Huber, Haupt, Preut, Barbieri & Lo Giudice, 1977; Huber, Vornefeld, Preut & von Angerer, 1990) the C—Sn—C angle is expanded to 128°; this is interesting because it is a similar value to that found in diethyltin glycytyrosinate, 131.4 (2)° (Vornefeld, Huber, Preut & Barbieri, 1990).

In molecule (2), in contrast to molecule (1) and all other structurally characterized diorganotin derivatives of dipeptides, tin has an octahedral surrounding which is rather distorted. O(21) and N(22) (= N_{amino}) are axially arranged; the equatorial positions are occupied by C(26), C(28), N(21) (= N_{peptide}), and by N(14) of the histidinyl group of molecule (1). The distance Sn(2)—N(14) of 2.790 (5) Å is rather long, but appreciably shorter than the sum of the van der Waals radii of Sn and N (3.62 Å; Bondi, 1964). The inference of bonding interaction between Sn(2) and N(14), which implicates linking of molecules (1) and (2) to form a dimer, is also justified by considering the values of the angles O(21)—Sn(2)—N(22) (axial) of 150.0 (2) and C(26)—Sn(2)—C(28) (equatorial) of

Table 2. Bond distances (Å), bond angles (°), least-squares planes and dihedral angles (°)

	$i = 1$	$i = 2$
O(11)—Sn(i)	2.181 (4)	2.238 (4)
N(11)—Sn(i)	2.102 (5)	2.132 (4)
N(12)—Sn(i)	2.271 (5)	2.266 (5)
C(18)—Sn(i)	2.130 (8)	2.130 (7)
C(16)—Sn(i)	2.132 (7)	2.128 (7)
C(11)—O(11)	1.281 (8)	1.267 (7)
C(11)—O(12)	1.242 (7)	1.245 (7)
C(11)—C(12)	1.510 (9)	1.538 (8)
C(12)—N(11)	1.453 (7)	1.467 (7)
C(12)—C(15)	1.561 (9)	1.533 (9)
C(13)—O(13)	1.245 (8)	1.242 (7)
C(13)—N(11)	1.318 (8)	1.315 (7)
C(13)—C(14)	1.493 (9)	1.515 (8)
C(14)—N(12)	1.480 (9)	1.467 (8)
C(11)—N(13)	1.394 (7)	1.381 (9)
C(11)—C(112)	1.359 (8)	1.382 (9)
C(11)—C(15)	1.481 (8)	1.478 (9)
C(112)—N(14)	1.381 (8)	1.365 (10)
C(113)—N(13)	1.357 (8)	1.361 (9)
C(113)—N(14)	1.304 (8)	1.262 (11)
C(16)—C(17)	1.476 (14)	1.472 (13)
C(18)—C(19)	1.527 (10)	1.520 (10)
C(1)—O(1)	1.311 (13)	(Methanol)
N(11)—Sn(i)—O(11)	75.6 (2)	74.4 (2)
N(12)—Sn(i)—O(11)	151.9 (2)	150.0 (2)
N(12)—Sn(i)—N(11)	76.4 (2)	76.2 (2)
C(18)—Sn(i)—O(11)	92.3 (2)	87.1 (2)
C(18)—Sn(i)—N(11)	112.9 (2)	105.3 (2)
C(18)—Sn(i)—N(12)	96.3 (3)	96.3 (2)
C(16)—Sn(i)—O(11)	94.7 (2)	88.8 (2)
C(16)—Sn(i)—N(11)	118.0 (3)	103.6 (2)
C(16)—Sn(i)—N(12)	100.5 (2)	103.8 (2)
C(16)—Sn(i)—C(18)	128.7 (3)	148.5 (3)
C(11)—O(11)—Sn(i)	117.4 (4)	118.7 (4)
C(12)—N(11)—Sn(i)	118.6 (4)	119.1 (3)
C(13)—N(11)—Sn(i)	120.3 (4)	120.1 (4)
C(14)—N(12)—Sn(i)	110.7 (4)	111.5 (3)
C(19)—C(18)—Sn(i)	110.2 (6)	111.7 (5)
C(17)—C(16)—Sn(i)	115.1 (6)	114.1 (6)
O(12)—C(11)—O(11)	121.7 (6)	124.3 (6)
C(12)—C(11)—O(11)	118.8 (5)	117.9 (5)
C(12)—C(11)—O(12)	119.5 (6)	117.8 (5)
C(11)—C(12)—N(11)	109.6 (5)	109.9 (4)
C(15)—C(12)—N(11)	113.6 (5)	113.9 (5)
C(15)—C(12)—C(11)	110.5 (5)	110.1 (5)
N(11)—C(13)—O(13)	125.1 (5)	126.9 (5)
C(14)—C(13)—O(13)	115.5 (5)	117.0 (5)
C(14)—C(13)—N(11)	117.5 (5)	115.9 (5)
C(13)—C(14)—N(12)	113.9 (5)	114.3 (5)
C(13)—N(11)—C(12)	120.0 (5)	118.6 (4)
C(11)—C(15)—C(12)	113.4 (5)	115.6 (5)
C(15)—C(11)—N(13)	121.0 (5)	133.2 (6)
N(14)—C(113)—N(13)	112.0 (6)	105.8 (6)
C(112)—C(111)—N(13)	104.3 (5)	103.7 (6)
C(112)—C(111)—C(15)	134.6 (5)	123.1 (5)
C(111)—C(112)—N(14)	111.3 (5)	106.4 (6)
C(113)—N(13)—C(111)	107.2 (5)	110.9 (6)
C(113)—N(14)—C(112)	105.2 (5)	113.2 (7)

Plane through atoms	Equation of the plane
Number	(x along a; y in the plane ab; z along c)
1 Sn(1), O(11), C(11), C(12), N(11) C(13), C(14), N(12)	+0.3102x - 0.3881y - 0.8679z = -11.863 Å
2 Sn(1), O(11), C(11), C(12), N(11)	+0.2701x - 0.4341y - 0.8594z = -11.948 Å
3 Sn(1), N(11), C(13), C(14), N(12)	+0.30657x - 0.36734y - 0.8781z = -12.045 Å
4 C(111), C(113), N(13), N(14)	+0.9434x + 0.1854y - 0.2752z = -2.518 Å
Dihedral angles: 1, 2 3.5 (1); 1, 3 1.3 (1); 1, 4 62.6 (2); 2, 3 4.5 (1); 2, 4 65.7 (2); 3, 4 62.4 (2)°.	
Plane through atoms	Equation of the plane
Number	(x along a; y in the plane ab; z along c*)
1 Sn(2), O(21), C(21), C(22), N(21) C(23), C(24), N(22)	+0.9055x + 0.4193y - 0.0658z = -2.013 Å
2 Sn(2), O(21), C(21), C(22), N(21)	+0.8744x + 0.4839y - 0.0356z = -1.585 Å
3 Sn(2), N(21), C(23), C(24), N(22)	+0.9223x + 0.3848y - 0.0372z = -1.946 Å
4 C(212), C(213), N(23), N(24)	+0.2165x + 0.3016y - 0.9285z = -10.314 Å
Dihedral angles: 1, 2 4.5 (1); 1, 3 2.7 (1); 1, 4 67.4 (2); 2, 3 6.3 (1); 2, 4 68.4 (2); 3, 4 69.5 (3)°.	

148.5 (3)° both of which demonstrate the opening of the coordination sphere around tin for accommodating a sixth ligand. The corresponding equatorial

C—Sn—C angle in molecule (1) is 128.7 (3)° approaching the ideal value in a trigonal bipyramid. From short N...O distances the presence of H bonds is inferred. They are in some cases markedly shorter than the sum of the van der Waals radii (3.11 Å; Kitaigorodskii, 1979). Thus, intermolecular distances N(12)...O(13) of 2.768 Å and intramolecular distances N(22)...O(22) of 3.029 Å, and N(12)...O(12) of 2.998 Å are observed. It is noteworthy that the MeOH molecule is independent and is not involved in the hydrogen-bonding system.

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References

- ALCOCK, N. W. & SAWYER, J. F. (1977). *J. Chem. Soc. Dalton Trans.* pp. 1090–1095.
- BONDI, A. (1964). *J. Phys. Chem.* **68**, 441–451.
- HUBER, F. & BARBIERI, R. (1986). *Tin as a Vital Nutrient: Implications in Cancer Prophylaxis and Other Physiological Processes*, edited by N. F. CARDARELLI, pp. 175–187. Boca Raton, Florida: CRC Press.
- HUBER, F., HAUPT, H. J., PREUT, H., BARBIERI, R. & LO GIUDICE, M. T. (1977). *Z. Anorg. Chem.* **432**, 51–57.
- HUBER, F., MUNDUS, B., BARBIERI, R. & RUISI, G. (1986). *Atti Convegno Naz. Mössbauer, Alghero*, pp. 67–74.
- HUBER, F., VORNEFELD, M., PREUT, H. & VON ANGERER, E. (1990). *Appl. Organomet. Chem.* In the press.
- KITAIGORODSKII, A. I. (1979). *Molekülkristalle*, pp. 17–19. Berlin: Akademie-Verlag.
- NARDELLI, M. (1983). *Comput. Chem.* **7**, 95–98.
- PREUT, H., MUNDUS, B., HUBER, F. & BARBIERI, R. (1986). *Acta Cryst.* **C42**, 536–538.
- PREUT, H., MUNDUS, B., HUBER, F. & BARBIERI, R. (1989). *Acta Cryst.* **C45**, 728–730.
- ROGERS, D. (1981). *Acta Cryst.* **A37**, 734–741.
- SHELDRIK, G. M. (1976). *SHELX76*. A program for crystal structure determination. Univ. of Cambridge, England.
- SHELDRIK, G. M. (1987). *SHELXTL-Plus*. Release 3.4 for Nicolet R3m/V crystallographic system. Nicolet Instrument Corporation, Madison, Wisconsin, USA.
- VORNEFELD, M., HUBER, F., PREUT, H. & BARBIERI, R. (1990). In preparation.
- WILLIAMS (1984). *PCK83*. Quantum Chemistry Program Exchange. No. 481. Univ. of Indiana, USA.

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Structures of the Mixed-Metal Carboxylate Base Adducts [MgZn₂(crotonate)₆(4-vinylpyridine)₂] and [MgCo₂(crotonate)₆(4-vinylpyridine)₄]

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Abstract. (1) [MgZn₂(C₄H₅O₂)₆(C₇H₇N)₂], $M_r = 875.8$, monoclinic, $P2_1/c$, $a = 10.251$ (1), $b = 14.315$ (2), $c = 14.382$ (2) Å, $\beta = 106.52$ (1)°, $V = 2023.4$ Å³, $Z = 2$, $D_x = 1.437$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 12.9$ cm⁻¹, $F(000) = 908$, $T = 295$ K, $R = 0.063$ for 2829 unique observed reflections. (2) [MgCo₂(C₄H₅O₂)₆(C₇H₇N)₄], $M_r = 1073.2$, monoclinic, $C2/c$, $a = 24.623$ (2), $b = 11.855$ (1), $c = 18.855$ (1) Å, $\beta = 104.640$ (6)°, $V = 5325.2$ Å³, $Z = 4$, $D_x = 1.338$ g cm⁻³, $\mu(\text{Mo } K\alpha) = 6.9$ cm⁻¹, $F(000) = 2240$, $T = 295$ K, $R = 0.030$ for 3709 unique observed reflections. The molecules contain an exactly (1) or approximately (2) linear array of three metal atoms linked by six crotonate bridges. Four of the bridges are of the *syn-syn* type, coordinating to one metal atom through each of their two O atoms. The other two crotonates are simultaneously chelating to one metal (Zn or Co) and bridging through

one O atom also to Mg. In (1), Zn is five-coordinate, and in (2), Co is six-coordinate, with one or two 4-vinylpyridine terminal ligands respectively. The Mg atom is octahedrally coordinated in both structures.

Introduction. The first crystal structure of a trinuclear metal carboxylate complex of formula [MM'₂(O₂CR)₆L₂] was reported by Catterick, Hursthouse, New & Thornton (1974): in this case, all three metal atoms were cobalt. Several other compounds of this kind have been studied since then, with $M' = \text{Zn}$ and a variety of different central metals $M = \text{Zn}$, Mn, Co, Ni, Cd, Mg, Ca, Sr, Ba; L is a heterocyclic nitrogen base, and the carboxylates include benzoate, crotonate and pivalate (Clegg, Little & Straughan, 1985, 1986, 1988; Clegg, Hunt, Straughan & Mendiola, 1989; Catterick & Thornton, 1976). In each case, the three metal atoms are arranged in a linear