Stereochemistry of Flexible-chelate–Metal Complexes. Part III.[1] Crystal Structure of Dihydrogen Ethylenediaminetetra-acetatostannate(II)

By **K. G. Shields, R. C. Seccombe,** and **C. H. L. Kennard,*** Department of Chemistry, University of Queensland, Brisbane, Queensland, 4067, Australia

The crystal structure of the title compound has been determined from three-dimensional diffractometer data. The orthorhombic unit cell, space group *Pbca*, has dimensions a = 659·1(1), b = 1303·1(2), c = 3221·6(6) pm, and Z = 8. The structure was solved by Patterson and Fourier methods, refined by least squares to R 0·056 for 2130 observed reflections. The tin atom is centred in the rectangular face of a distorted triangular prism (Sn–N 238·8 and 244·2, Sn–O 219·6, 234·3, 263·5, and 305·7 pm). Intermolecular hydrogen bonds link carboxy-groups from differing molecules forming a one-dimensional polymer in the *b* direction.

In the quest for a compound where ethylenediaminetetra-acetic acid (edta) is quadridentate, the structure of dihydrogen ethylenediaminetetra-acetatostannate(II) has been determined.

A number of different co-ordination arrangements have been found recently for this ligand. In sodium hexaoxo-μ-ethylenediaminetetra-acetato-dimolybdate-(VI) octahydrate,[2] edta bridges two molybdenum trioxide groups with molybdenum(VI) having a co-ordination number of six. The edta is fully complexed, with the two carboxylate groups attached to the metal in a *cis*-configuration from an apical nitrogen.

Quadridentate edta is found in ammonium (dihydrogenethylenediaminetetra-acetato)dioxovanadate(V) trihydrate,[3] and trisodium (ethylenediaminetetra-acetato)-dioxovanadate(V) tetrahydrate.[4] The two carboxylate groups from different nitrogens are co-ordinated to the octahedral vanadium atom through polar oxygens. Oxo-ligands are in the remaining two positions.

The ligand edta is sexidentate in (ethylenediaminetetra-acetato)tin(II) monohydrate,[5] [Sn(edta),H_2O] (Sn–N 229·6 and 232·9, Sn–O 207·4, 207·5, 208·8, and 209·3, Sn–H_2O 212·4 pm), where the metal is seven-co-ordinate.

Tin(II) (ethylenediaminetetra-acetatostannate(II) dihydrate,[6] Sn[Sn(edta)],2H_2O, has a distorted pentagonal bipyramid co-ordination around the tin atom, where the ethylenediamine nitrogens and the tin lone-electron-pair occupy equatorial positions (Sn–N 245 and 246, Sn–O_g, 264 and 270, Sn–O_r 229 and 245 pm).†

In the present complex, dihydrogen ethylenediaminetetra-acetatostannate(II) (Figure 1), the tin is centered in the rectangular face of a distorted triangular prism (Sn–N 238·8 and 244·2, Sn–O 219·6, 234·3, 263·5, and 305·7 pm) (Table 1). This compound was prepared by the addition of disodium ethylenediaminetetra-acetate to tin(II) chloride at pH 1·5.

An assignment of the carboxy i.r. spectrum suggests [7] the presence of both free and complexed carboxy-groups indicating that edta behaves as a quadridentate ligand. In this case, in terms of a Sn–O distance of 213—240 pm,[8] edta chelates as a quadridentate ligand. However, there are weak but definite links to two other oxygens: Sn–O(19) 263·5 and Sn–O(15) 305·1 pm.

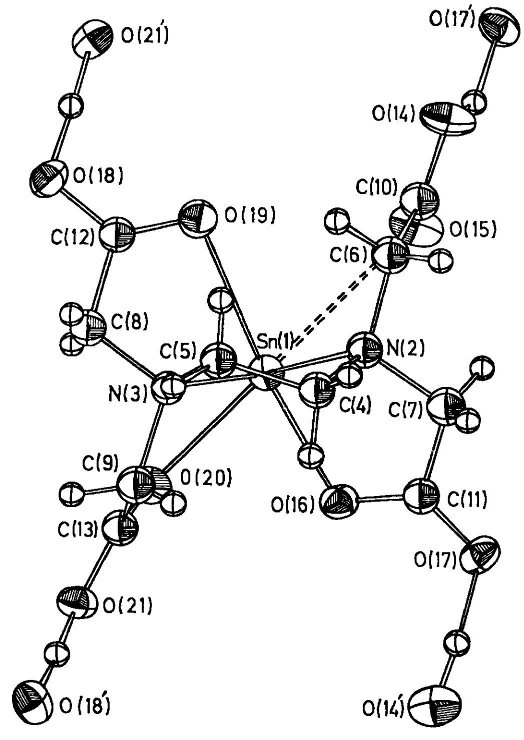

FIGURE 1 The structure viewed along the bisector of the N–Sn–N angle

This does not explain completely the i.r. spectrum, because there is little relationship between the long metal–oxygen distance and a proton on the same acid group. However, it is difficult to locate accurately hydrogen atoms in metal complexes. These particular atoms, H(34) and H(35), were found at the conclusion of the refinement.

---

† The *g* refers to the five membered acetato-metal ring in the plane of the ethylenediamine ring, while *r* is the one perpendicular.

[1] Part II, D. J. Robinson and C. H. L. Kennard, *J. Chem. Soc.* (*A*), 1970, 1008.

[2] J. J. Park, M. D. Glick, and J. L. Hoard, *J. Amer. Chem. Soc.*, 1969, **91**, 301.

[3] W. R. Scheidt, D. M. Collins, and J. L. Hoard, *J. Amer. Chem. Soc.*, 1971, **93**, 3873.

[4] W. R. Scheidt, R. Countryman, and J. L. Hoard, *J. Amer. Chem. Soc.*, 1971, **93**, 3878.

[5] F. P. van Remoortere, J. J. Flynn, and F. P. Boer, *Inorg. Chem.*, 1971, **10**, 2313.

[6] F. P. van Remoortere, J. J. Flynn, F. P. Boer, and P. P. North, *Inorg. Chem.*, 1971, **10**, 1511.

[7] R. N. Lebedeva, E. M. Yakimets, and E. F. Emlin, *Russ. J. Inorg. Chem.*, 1967, **12**, 575.

[8] J. D. Donaldson, *Progr. Inorg. Chem.*, 1967, **8**, 287.

In the same way, edta in $Sn[Sn(edta)],2H_2O$ acts as a tetradentate through the O_r and not the O_g. The main difference between these two tin–edta complexes centres around the rotation of the acetato-arms about the nitrogen atoms. In the dihydrate, there are two definite O_r and two O_g arms. However, in the acid complex, these arms are approximately equivalent and similar to those in the manganese structure.[9]

TABLE 1

(*a*) Interatomic distances (pm) with estimated standard deviations given in parentheses

Sn–N(2)	244·2(5)	C(12)–O(18)	129·1(8)
Sn–N(3)	238·8(5)	C(12)–O(19)	122·0(8)
Sn–O(15)	305·7(5)	C(13)–O(20)	127·0(8)
Sn–O(16)	219·6(5)	C(13)–O(21)	125·0(8)
Sn–O(19)	263·5(5)	C(4)–H(24)	94
Sn–O(20)	234·3(5)	C(4)–H(25)	100
N(2)–C(4)	147·8(8)	C(5)–H(22)	90
N(2)–C(6)	147·2(8)	C(5)–H(23)	107
N(2)–C(7)	148·6(8)	C(6)–H(32)	106
N(3)–C(5)	149·7(8)	C(6)–H(33)	92
N(3)–C(8)	146·9(8)	C(7)–H(30)	102
N(3)–C(9)	148·3(8)	C(7)–H(31)	86
C(4)–C(5)	149·4(9)	C(8)–H(28)	76
C(6)–C(10)	150·4(9)	C(8)–H(29)	95
C(7)–C(11)	151·5(10)	C(9)–H(26)	65
C(8)–C(12)	152·1(9)	C(9)–H(27)	96
C(9)–C(13)	151·7(9)	O(14)–H(34)	99
C(10)–O(14)	132·6(9)	O(17)–H(34)	170
C(10)–O(15)	120·0(9)	O(18)–H(35)	129
C(11)–O(16)	128·2(8)	O(21)–H(35)	126
C(11)–O(17)	122·7(8)		

(*b*) Interatomic angles (°) with estimated standard deviations in parentheses

N(2)–Sn–N(3)	73·86(13)	N(2)–C(6)–C(10)	113·7(4)
N(2)–Sn–O(15)	59·85(9)	N(2)–C(6)–H(32)	111
N(2)–Sn–O(16)	69·74(18)	N(2)–C(6)–H(33)	106
N(2)–Sn–O(19)	80·53(15)	C(10)–C(6)–H(32)	108
N(2)–Sn–O(20)	129·82(16)	C(10)–C(6)–H(33)	108
N(3)–Sn–O(15)	119·69(16)	H(32)–C(6)–H(33)	110
N(3)–Sn–O(16)	92·2(2)		
N(3)–Sn–O(19)	65·1(2)	N(2)–C(7)–C(11)	111·1(4)
N(3)–Sn–O(20)	69·5(2)	N(2)–C(7)–H(30)	106
O(15)–Sn–O(16)	104·5(2)	N(2)–C(7)–H(31)	103
O(15)–Sn–O(19)	70·8(2)	C(11)–C(7)–H(30)	107
O(15)–Sn–O(20)	169·8(2)	C(11)–C(7)–H(31)	108
O(16)–Sn–O(15)	146·9(2)	H(30)–C(7)–H(31)	122
O(16)–Sn–O(20)	78·5(2)	N(3)–C(8)–C(12)	111·6(4)
O(19)–Sn–O(20)	112·1(2)	N(3)–C(8)–H(28)	101
		N(3)–C(8)–H(29)	102
Sn–N(2)–C(4)	107·1(3)	C(12)–C(8)–H(28)	91
Sn–N(2)–C(6)	117·5(3)	C(12)–C(8)–H(29)	104
Sn–N(2)–C(7)	103·3(3)	H(28)–C(8)–H(29)	146
C(4)–N(2)–C(6)	109·1(4)	N(3)–C(9)–C(13)	112·7(4)
C(4)–N(2)–C(7)	109·3(4)	N(3)–C(9)–H(26)	99
C(6)–N(2)–C(7)	110·3(4)	N(3)–C(9)–H(27)	117
Sn–N(3)–C(5)	111·1(3)	C(13)–C(9)–H(26)	105
Sn–N(3)–C(8)	108·2(3)	C(13)–C(9)–H(27)	84
Sn–N(3)–C(9)	108·1(3)	H(26)–C(9)–H(27)	137
C(5)–N(3)–C(8)	110·2(4)	C(6)–C(10)–O(14)	110·1(5)
C(5)–N(3)–C(9)	109·9(4)	C(6)–C(10)–O(15)	124·2(5)
C(8)–N(3)–C(9)	109·3(4)	O(14)–C(10)–O(15)	125·7(6)
N(2)–C(4)–C(5)	111·2(4)	C(7)–C(11)–O(16)	116·9(4)
N(2)–C(4)–H(24)	109	C(7)–C(11)–O(17)	117·6(5)
N(2)–C(4)–H(25)	111	O(16)–C(11)–O(17)	125·4(5)
C(5)–C(4)–H(24)	103		
C(5)–C(4)–H(25)	110	C(8)–C(12)–O(18)	114·1(5)
H(24)–C(4)–H(25)	112	C(8)–C(12)–O(19)	120·9(5)
		O(18)–C(12)–O(19)	124·9(5)
N(3)–C(5)–C(4)	111·1(4)	C(9)–C(13)–O(20)	117·3(5)
		C(9)–C(13)–O(21)	119·0(4)
N(3)–C(5)–H(22)	107	O(20)–C(13)–O(21)	123·7(5)
N(3)–C(5)–H(23)	102	Sn–O(15)–C(10)	104·3(3)
C(4)–C(5)–H(22)	104	Sn–O(16)–C(11)	118·1(3)
C(4)–C(5)–H(23)	121	Sn–O(19)–C(12)	105·7(3)
H(22)–C(5)–H(23)	110	Sn–O(20)–O(13)	117·3(3)

In solution, the edta probably acts as a quadridentate ligand with the tin out of a square planar arrangement. No doubt in the solid state, the free carboxy-groups are attracted by the available orbitals of the metal atom and form weak links.

Intermolecular hydrogen bonds link carboxy-groups from differing molecules forming a one-dimensional polymer in the *b* direction (Figure 2).

EXPERIMENTAL

Crystal Data.—$C_{10}H_{14}N_2O_8Sn$, $M = 408{\cdot}9$, Orthorhombic, $a = 659{\cdot}1(1)$, $b = 1303{\cdot}1(2)$, $c = 3221{\cdot}6(6)$, $U = 2{\cdot}767$ nm^3, $Z = 8$, $D_c = 1{\cdot}95$, $F(000) = 1616$. Space group $Pbca(D_{2h}^{15}$, No. 61). Mo-K_α radiation, $\lambda = 71{\cdot}07$ pm.

TABLE 2

Atomic positions (fractional co-ordinates) and temperature factors with estimated standard deviations in parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*/Å^2
Sn	0·63856(6)	0·18331(3)	0·36794(1)	*
N(2)	0·8716(8)	0·2618(4)	0·4176(2)	2·0(1)
N(3)	0·8335(7)	0·3053(4)	0·3296(2)	1·8(1)
C(4)	0·9375(10)	0·3607(5)	0·3996(2)	2·0(1)
C(5)	1·0018(10)	0·3483(5)	0·3555(2)	2·1(1)
C(6)	1·0518(10)	0·2023(5)	0·4298(2)	2·2(1)
C(7)	0·7410(10)	0·2816(5)	0·4543(2)	2·3(1)
C(8)	0·9165(10)	0·2534(5)	0·2928(2)	2·3(1)
C(9)	0·6957(10)	0·3889(5)	0·3162(2)	2·2(1)
C(10)	1·0074(11)	0·0915(5)	0·4391(2)	2·4(1)
C(11)	0·5315(10)	0·3169(5)	0·4413(2)	2·2(1)
C(12)	0·9988(11)	0·1476(5)	0·3034(2)	2·2(1)
C(13)	0·4846(10)	0·3507(5)	0·3055(2)	2·0(1)
O(14)	1·1742(7)	0·0446(4)	0·4522(2)	*
O(15)	0·8449(7)	0·0517(4)	0·4342(2)	*
O(16)	0·4835(6)	0·3046(4)	0·4031(1)	*
O(17)	0·4212(7)	0·3538(4)	0·4682(1)	*
O(18)	1·0727(8)	0·0984(4)	0·2721(1)	*
O(19)	0·9850(8)	0·1133(3)	0·3386(1)	*
O(20)	0·4398(7)	0·2596(3)	0·3162(1)	*
O(21)	0·3657(7)	0·4091(3)	0·2866(2)	*
H(22)	1·1000 †	0·3000	0·3563	2·0
H(23)	1·0500	0·4125	0·3375	2·0
H(24)	0·8250	0·4050	0·3975	2·0
H(25)	1·0500	0·3925	0·4163	2·0
H(26)	0·6850	0·4125	0·3337	2·0
H(27)	0·7000	0·4075	0·2875	2·0
H(28)	0·8200	0·2300	0·2837	2·0
H(29)	1·0350	0·2925	0·2875	2·0
H(30)	0·7250	0·2125	0·4687	2·0
H(31)	0·8000	0·3325	0·4663	2·0
H(32)	1·1650	0·2050	0·4063	2·0
H(33)	1·1000	0·2325	0·4537	2·0
H(34)	1·1000	−0·0175	0·4612	2·0
H(35)	1·1100	0·0032	0·2800	2·0

† These parameters were not refined.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sn	1050(11)	265(3)	57(1)	−71(5)	18(2)	1(1)
O(14)	121(12)	40(3)	14(1)	16(5)	−10(2)	1(1)
O(15)	142(12)	36(3)	12(1)	−14(5)	−11(2)	1(1)
O(16)	95(11)	42(3)	7(1)	7(5)	−1(2)	−2(1)
O(17)	144(12)	37(3)	7(1)	1(5)	12(2)	−1(1)
O(18)	171(13)	41(3)	6(1)	16(5)	10(2)	−1(1)
O(19)	218(14)	28(3)	6(1)	5(5)	5(2)	−1(1)
O(20)	125(11)	28(3)	8(1)	−13(5)	−2(2)	1(1)
O(21)	123(11)	33(3)	7(1)	14(5)	−7(2)	−2(1)

* Anisotropic thermal parameters (×10^4, Sn ×10^5) in the form: $\exp -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$.

Angle data, from a crystal mounted about the *a* axis,

---

[9] S. Richards, B. Pedersen, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, 1964, **3**, 27.

were measured from six Friedel pairs and used to obtain accurate unit-cell dimensions by a least-squares procedure. Of 2450 independent reflections measured on a Hilger and Watts computer-controlled four-circle diffractometer by use of a 2θ—ω step scan up to a θ value of 26°, 2130 were considered observed, having $I > 2{\cdot}5\sigma(I)$. Data were collected at a constant scan rate of 0·01° s^{-1}, and a scan-width of 1° in 2θ.

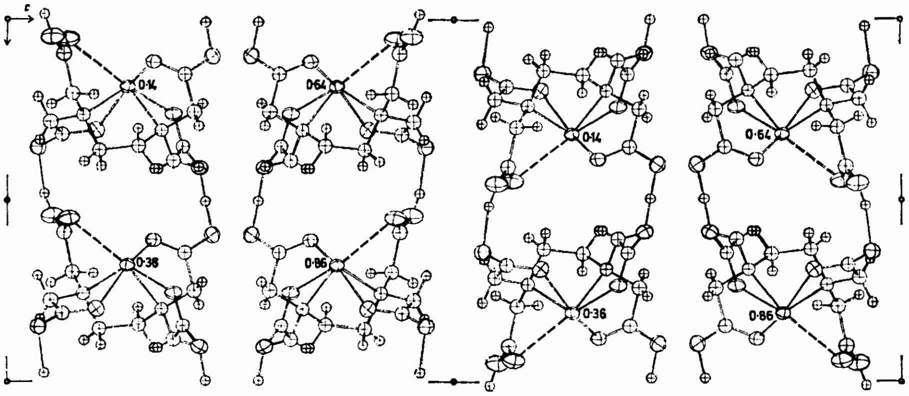

FIGURE 2 Packing of the molecule viewed perpendicular to *a*

Structure Determination and Refinement.—The tin atom was located from a Patterson synthesis. By use of the tin co-ordinates, an electron-density calculation revealed all the non-hydrogen atom positions. The hydrogen atoms were located from a difference-Fourier synthesis. The final least-squares cycle reduced R to 0·056 and R' to 0·054 $\{R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$. A final difference-Fourier synthesis revealed no unaccounted electron density. Atomic and thermal parameters are given in Table 2.

A list of observed and calculated structure amplitudes (×10) appears in Supplementary Publication No. SUP 20622 (8 pp., 1 microfiche).*

Atomic scattering factors for tin, oxygen, nitrogen, carbon, and hydrogen, were taken from ref. 10 with a correction for anomalous dispersion[10] applied to the tin atom. The structure was determined, refined, and bond distances calculated with local versions of standard programs.[11]

We thank Professor B. Penfold, University of Canterbury, for making available the diffractometer, and Dr. W. Robinson for this assistance during data collection. K. G. S. and R. C. S. are supported by Commonwealth Postgraduate Scholarships.

[2/2081 *Received, 4th September,* 1972]

---

* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

[10] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962, pp. 202—216.

[11] PREFOUR, Structure Factor; FOURIER, J. Blount, 1966; ORFLS, Full-matrix Least-Squares, W. R. Busing, K. O. Martin, and H. A. Levy, Oak Ridge National Laboratory, ORNL TM 305, 1962; ORTEP, C. J. Johnson Oak Ridge National Laboratory, ORNL 3794, 1965.