Inorganica Chimica Acta, 30 (1978) L321–L323
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Complexes of Organometallic Compounds. XLIX. A Mössbauer–Zeeman Spectroscopic Study of Glycylglycinato-O,N,N(2–) Diphenyltin(IV), and the Point-charge Model Rationalization of the Quadrupole Splittings of Some Glycylglycinato-O,N,N(2–) Diorganotin(IV) Complexes

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Received June 27, 1978

Novel complexes of Alk_2Sn^{IV} moieties with glycylglycine in the dianionic form, formulated as glycylglycinato-O,N,N(2–) dialkyltin(IV), Alk_2Sn(Gly-Gly), have been recently reported [1]. Their configuration has been assumed to be of trigonal bipyramidal type, with carbon atoms bound to tin located in the trigonal plane, on the basis of magnitude of their Mössbauer parameters, nuclear quadrupole splittings, ΔE [1]. By X-ray diffractometry it has been subsequently demonstrated that this structure is present in Ph_2Sn(Gly-Gly) [2]. Then, it seemed opportune to further rationalize the configurational hypothesis on Alk_2Sn(Gly-Gly), chosing to the purpose the point charge model treatment of experimental ΔE's [3]. The latter work is reported in the present letter.

The Mössbauer–Zeeman spectrum of Ph_2Sn(Gly-Gly) has been determined (Fig. 1), from which ΔE with its proper sign, as well as the asymmetry parameter $\eta = \frac{V_{xx} - V_{yy}}{V_{zz}}$, have been obtained [4] and are reported in Table I. Point charge model estimates of these parameters have been extracted for the ideal trigonal bipyramidal structure of Fig. 2, using Eqns. (1–3) for calculating $V_{\alpha\alpha}$ (the principal components of the electric field gradient tensor at the Sn nucleus) and Eqn. (4) for ΔE [3–5]:

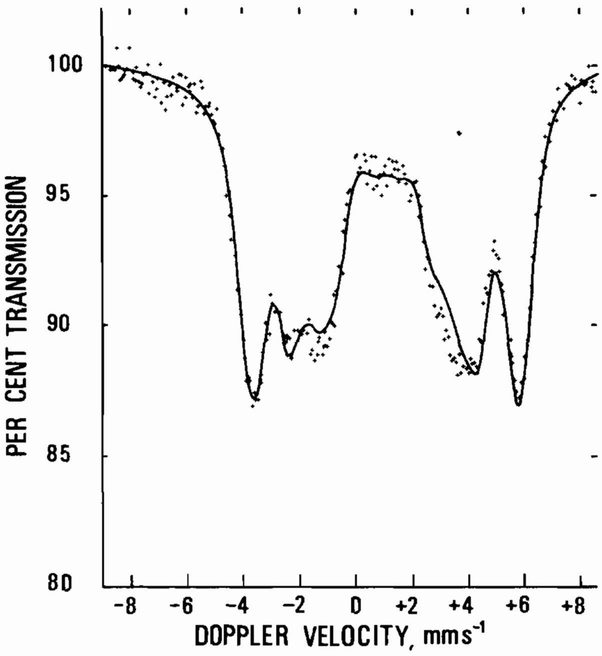

Figure. 1. The Mössbauer–Zeeman spectrum of Ph_2Sn(Gly-Gly), determined at 4.2 °K in a transversal magnetic field of 6 T by P.C.M.U., Harwell. Full line is the computer fitting of experimental points.

$$V_{kk} = -2[Ph]^{tbe} - [N]^{tbe} + 2[O]^{tba} + 2[N]^{tba} \qquad (1)$$

$$V_{jj} = \frac{5}{2}[Ph]^{tbe} - [N]^{tbe} - [O]^{tba} - [N]^{tba} \qquad (2)$$

$$V_{xx} = -\frac{1}{2}[Ph]^{tbe} + 2[N]^{tbe} - [O]^{tba} - [N]^{tba} \qquad (3)$$

TABLE I. Experimental Quadrupole Splittings, ΔE, Asymmetry Parameter, η, and Point Charge Model Estimates.

Compound[a]	ΔE_{exp}, mm s^{-1}	Refs.	ΔE^{b}_{calcd}	η^{b}_{calcd}
Ph_2Sn(Gly-Gly)[c]	–2.235 (η = 0.805)	d	(–) 2.70	0.84
Me_2Sn(Gly-Gly)	3.29	1	(–) 3.09	0.91
Bu^n_2Sn(Gly-Gly)	3.19	1		
Oct^n_2Sn(Gly-Gly)	3.43	1		

[a] Gly-Gly is glycylglycinato-O,N,N(2–). [b] For a regular trigonal bipyramidal structure, Fig. 2. P.q.s.'s values, mm s^{-1}, used in the calculations are [3]: $\{Ph\}^{tbe} = -0.98$; $\{Alk\}^{tbe} = -1.13$; $\{N\}^{tbe} = -0.30$ (see text); $\{O\}^{tba} = +0.075$ (*i.e.*, the p.q.s. of axially coordinated acetic acid [3]); $\{N\}^{tba} = +0.01$ (the p.q.s. of axial piperidine [3]). [c] Isomer shift with respect to R.T. $CaSnO_3$ is $\delta = 1.037$ mm s^{-1}. [d] This work.

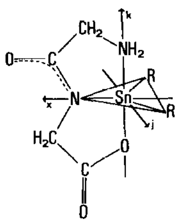

Figure 2. The idealized trigonal bipyramidal configuration of $Ph_2Sn(Gly\text{-}Gly)$, corresponding to the real molecular structure [2], assumed also for $Alk_2Sn(Gly\text{-}Gly)$. x, j, k are the principal components of the e.f.g. tensor (see text).

$$\Delta E = \frac{1}{2} e^2 Q V_{zz} \left(1 + \frac{\eta^2}{3}\right)^{\frac{1}{2}} \qquad (4)$$

Q is the quadrupole moment of the nucleus, negative for ^{119}Sn, so that the signs of V_{zz} and ΔE are opposite. Partial quadrupole splittings, p.q.s., used in the calculations of $V_{\alpha\alpha}$ were expressed as follows [3]:

$$\{L\}^{tba} = \frac{1}{2} e^2|Q|([L]^{tba} - [Cl, Br]^{tba}), \text{mm s}^{-1} \qquad (5)$$

$$\{L\}^{tbe} = \frac{1}{2} e^2|Q|([L]^{tbe} - \frac{4}{3}[Cl, Br]^{tba}), \text{mm s}^{-1} \qquad (6)$$

where superscripts tba and tbe refer to trigonal bipyramidal axial and equatorial point charges, respectively [3]. Numerical values of $\{Ph\}^{tbe}$, $\{O,N\}^{tba}$ are reported in Table I, footnote c. The value $\{N\}^{tbe}$ = +0.21 was first selected, according to the relationship [3]:

$$3\{N\}^{tbe} - 4\{N\}^{tba} = 0.58 \text{ mm s}^{-1} \qquad (7)$$

The following data were calculated (k, j, x as in Fig. 2):

$$V_{zz} = V_{jj} = -2.74(5); V_{yy} = V_{kk} = +1.92;$$
$$V_{xx} = +0.82(5); \eta = 0.40; \Delta E = +2.82;$$

which are inconsistent with experimental (Table I). In particular, the negative sign of experimental ΔE implies that V_{zz} must be positive, *i.e.*, electronic charge is concentrated in the xy plane. In the point charge model formalism, this is realized by increasing the donating power of equatorial nitrogen (*i.e.*, giving negative values to $\{N\}^{tbe}$), other p.q.s.'s being invariant. Inversion of the sign of ΔE takes place for $\{N\}^{tbe}$ between −0.20 and −0.25 mm s^{-1}, when $V_{kk} = V_{zz}$ and $V_{jj} = V_{yy}$ (Fig. 2); a reasonable set of ΔE and η values was obtained for $\{N\}^{tbe} = -0.30$ mm s^{-1} (Table I).

A slightly better accordance of calculated with experimental ΔE and η was reached by a computer procedure [6] using the actual crystallographic angles at tin in $Ph_2Sn(Gly\text{-}Gly)$ [2]. For example, with $\{Ph\}^{tbe}$ and $\{N,O\}^{tba}$ as in Table I, footnote c, and $\{N\}^{tbe} = -0.25$ mm s^{-1}, it results $\Delta E = -2.64$ and $\eta = 0.84$ (p.q.s.'s being considered absolute). This limited improvement depends on the quasi-regular structure of the trigonal plane in $Ph_2Sn(Gly\text{-}Gly)$ [2], as well as from the fact that apical p.q.s.'s used here, being nearly zero, would not substantially alter the calculated data whether axial distortions [2] are taken into account. It is also obvious that further improvements may be obtained by decreasing axial p.q.s.'s while maintaining the difference ~−0.30 mm s^{-1} between $\{N,O\}^{tba}$ and $\{N\}^{tbe}$.

All things considered, we prefer to keep in the present context estimations according to the literal point charge model and a regular structure, using as far as possible p.q.s.'s extracted from ample selections of experimental data [3], which allows wide systematics [3]. It may be objected that in this way the accepted limiting difference of 0.4 mm s^{-1} between ΔE_{calcd} and ΔE_{exp} [3] is exceeded for $Ph_2Sn(Gly\text{-}Gly)$ (Table I). This is due to the fact that ΔE_{exp} of the latter compound, although not exceptional [7], is lesser than values commonly determined for Ph_2SnL_3 species [3, 8]; *i.e.*, the imbalance between axial and equatorial electrons is lesser than usual, for our compound.

At this point, the magnitude of $\{N\}^{tba}$ we selected here (−0.30 mm s^{-1}) has to be justified, being at variance with both the procedure suggested from obtaining $\{L\}^{tbe}$ from $\{L\}^{tba}$ (see in the preceding) and quoted $\{L\}^{tbe}$ data [3]. It is first observed that σ donor power of peptide nitrogen has to be larger than that of amino nitrogen (Fig. 2). In fact, the latter is easily shown by an empirical electronegativity equalization procedure [9] on the dianion $^{(-)}OOC{-}CH_2{-}N^{(-)}{-}CO{-}CH_2{-}NH_2$, for which a valence bond structure is considered with resonance in the peptide bonds only, in accordance with the crystallographic data of the coordinated ligand [2] (formal charges being $Q_{N_{pept}} = Q_{O_{pept}} = -0.50$, and bond orders 1.50 for $(C\overset{\cdots}{-}N)_{pept}$ and $(C\overset{\cdots}{-}O)_{pept}$. After equalization by the CHELEQ program [9], it is obtained $Q_{N_{pept}} = -0.46$ and $Q_{N_{amino}} = -0.20$, which means that equatorial N would release more negative charge into the neighborhood of tin than apical N, on coordination (Fig. 2). Besides the bond length $Sn{-}N_{pept}$ is quite short [2], which suggests a consistent s character in that bond as well as its involvement into the π-delocalization of the peptide group [2]. The latter circumstances would concentrate negative charge in the trigonal plane in the proximity of the tin nucleus, so that $\{N\}^{tbe}$ would be not very much different from $\{Ph\}^{tbe}$. Lastly, Mössbauer ΔE values of stannylamines $Alk_3SnNAlk_2$ and $Me_3SnN(CH_2)_n$ [10–12], four coordinate monomers [11] where Sn–N bonds correspond to $Sn{-}N_{pept}$ in $Ph_2Sn(Gly\text{-}Gly)$, suggest a noticeable release of negative charge from the $NAlk_2$ group to

Sn. The point charge model calculation of the p.q.s. due to $NAlk_2$ in regular tetrahedral [5] Alk_3SnAlk_2, $\Delta E = -0.95$ (average of eight data [10–12]) gives ½ $eq|Q|([NAlk_2]^{tet} - [hal]^{tet}) = -0.89$ mm s^{-1}, which differs by only 0.48 mm s^{-1} from p.q.s. of Alk^{tet} [5].

Having rationalized ΔE_{exp} and η of Ph_2Sn(Gly-Gly), and demonstrated the reliability of the p.q.s.'s employed in the related point charge model treatment, the corresponding parameters of Alk_2Sn(Gly-Gly) have been analogously calculated on the hypothesis of regular trigonal bipyramidal structures and are reported in Table I, $V_{\alpha\alpha}$ being as follows: $V_{zz} = V_{kk} = +2.73$, $V_{yy} = V_{jj} = -2.61$, $V_{xx} = -0.12$ (Fig. 2). The satisfactory agreement between ΔE_{exp} and ΔE_{calcd} (Table I) confirms the assumed structure [1]. It must be taken into account that the sign of ΔE for Alk_2Sn(Gly-Gly) could be inverted with respect to our estimate (negative, Table I) in the case the CSnC angle exceeds 120° [13, 14]. On the other hand, there are not *a priori* reasons to invoke such an opening of this angle in the present context. For example, in the trigonal bipyramidal complex Me_2Sn-(ONO), where ligand atoms belong to the dianion of 2-hydroxy-N-(2-hydroxybenzylidene)aniline, the angle CSnC enlarges to 138.25° [15] with respect to 121.4° in the corresponding Ph_2Sn^{IV} derivative [16] owing to intermolecular interactions through three-coordinating oxygen [15]. This seems unlikely for Alk_2Sn(Gly-Gly), provided in this compound the intermolecular H-bonding between amino nitrogen and carbonyl oxygens, taking place in Ph_2Sn(Gly-Gly) [2], is maintained.

It is concluded that the structure of Alk_2Sn(Gly-Gly) is very probably trigonal bipyramidal, such as that of the Ph_2Sn^{IV} derivative. The ligating behaviour of the dipeptide glycyl-glycine towards R_2Sn^{IV} moieties is then quite dissimilar from that of amino acids [17], owing to the acidity of the peptide hydrogen atom.

Acknowledgements

The financial supports by NATO (Grant No. 812), and C.N.R. (Roma) through a contract for international scientific cooperation, are gratefully acknowledged.

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