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Complexes of Organometallic Compounds.
XLV. Synthesis and Mössbauer Spectroscopy of Diorganotin(IV) Adenine Complexes

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In the context of a research project on complexes formed by bases, constituent of biological molecules, with organotin(IV) moieties,[1] we present here some preliminary results concerning diorganotin(IV) derivatives of adenine, R_2SnAd_2.

The complexes have been synthesized by 1:2 reaction of R_2SnCl_2 (1 mmol; R = Bu^n, Oct^n, Ph) with the adeninato anion (2 mmol, from adenine and $NaOCH_3$) in ethanol (for Alk_2Sn^{IV}) or methanol solution (for Ph_2Sn^{IV}, final volume about 25 ml); the white crystalline precipitates have been filtered off, washed, and recrystallized from ethanol. All operations have been carried out under dry N_2 atmosphere. The stoichiometry $R_2Sn(C_5H_4N_5)_2$ is clearly indicated by the analytical data in the Table.

The configuration of R_2SnAd_2 has been investigated by Mössbauer spectroscopy, operating as usual,[2] the $Ba^{119m}SnO_3$ source moving at constant acceleration (sawtooth waveform). The determined parameters, reported in the table, would at first suggest a tetrahedral type arrangement of bonding electrons around tin(IV); they are in fact consistent, for example, with those of $R_2Sn(OSiPh_3)_2$ (δ = 0.98 ÷ 1.19 mm s^{-1}; ΔE = 1.96 ÷ 2.45 mm s^{-1}).[3]

This hypothesis has been tested by treating ΔE values with the point-charge model formalism, according to which the quadrupole splitting of regular tetrahedral R_2Sn^{IV} species (Fig. 1a) is expressed by the Equation:[4]

$$\Delta E = \tfrac{1}{2}\, eQV_{zz} \left(1 + \frac{\eta^2}{3}\right)^{1/2} = 2.31 \{([R] - [hal])_{tet} - ([N] - [hal])_{tet}\} \qquad (1)$$

where symbols have the usual meaning;[4] the indetermination of ΔE sign comes from the fact that the asymmetry parameter η (= $(V_{xx} - V_{yy})/V_{zz}$) is unity (the electric field gradients $|V_{zz}|$ and $|V_{yy}|$ being equal, and V_{xx} = 0, for the structure of Fig. 1a). Employing the proper partial quadrupole splitting (p.q.s.) parameters ([R] – [hal])$_{tet}$ (in ½ e^2Q units[4,5]) and experimental ΔE, the p.q.s. ([N] – [hal])$_{tet}$ (*i.e.*, the contribution of monodentate adeninato(1–) to the electric field gradient tensor in a regular tetrahedral structure) was calculated by Eq. (1), obtaining the average value of –0.46 mm s^{-1} (in ½ e^2 |Q| units). This figure fits reasonably well to reported p.q.s.$_{tet}$ series. In fact, it would indicate that the "p" donor ability of Ad^{1-} is lesser than that of organic groups as well as of "ligands" bearing metal atoms (bound to Sn^{IV}), while larger than that pertaining to I, NCS and RCOO.[4,5] This seems reasonable, although there are no other known examples of p.q.s.$_{tet}$ due to heterocyclic nitrogen in a tetrahedral environment. The possible occurrence of monomolecular tetrahedral R_2SnAd_2 with unidentate adenine would be thus advanced. The latter ligand would behave as in $[Cu(H_2Ad)Br_2]^{2+}$, $[Co(H_2O)_4(HAd)_2]^{2+}$ and *cis*-$[Co(en)_2ClAd]^+$.[6] In conclusion, taking also into account the general coordinating properties of adenine and its derivatives,[7] the complexes studied here would be formulated as bis(adeninato-N^9)diorganotin(IV).

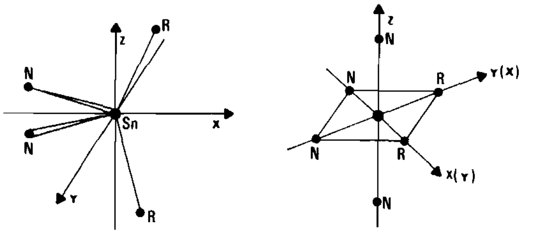

Fig. 1. Idealized distribution of donor atoms around Sn^{IV} in R_2SnAd_2 for : (a) tetrahedral and (b) *cis*-octahedral configurations. x,y,z are the principal components of the electric field gradient ($|V_{zz}| \gg |V_{yy}| \gg |V_{xx}|$); off-diagonal components of the e.f.g. tensor vanish in 1(a) and (b), *i.e.*, the tensor is diagonalized.

On the other hand, the Mössbauer parameters of R_2SnAd_2 would be consistent also with a *cis*-R_2 octahedral type structure around Sn^{IV}, falling typically in the ranges found for this configuration.[3b,4b] We further explored this possibility by treating ΔE of R_2SnAd_2, considered to assume the idealized geometry of Fig. 1b, with the point-charge model formalism, according to which the quadrupole splitting in this case would be expressed as follows:

$$(-)\,\Delta E = \tfrac{1}{2}\, eQV_{zz} = 2([N] - [hal])_{oct} - 2([R] - [hal])_{oct} \qquad (2)$$

being η = 0.[2,4] Operating as described above, and using the appropriate ([R] – [hal])$_{oct}$,[4,5] an average

TABLE. Analytical Data [% found(calcd)] and Mössbauer Parameters (mm s^{-1}, at liquid N_2 temperature).

Compound[a]	M.p. (°C)	C	H	N	Sn	δ[b]	ΔE[c]	Γav[d]
$Bu^{n}_{2}SnAd_2$	232 dec.	43.30 (43.14)	5.08 (5.23)	27.89 (27.95)	23.81 (23.68)	1.02	2.12	0.89
$Oct^{n}_{2}SnAd_2$	243 dec.	50.96 (50.91)	6.95 (6.90)	22.70 (22.84)	19.45 (19.35)	0.99	2.00	1.02
Ph_2SnAd_2	>350	48.84 (48.83)	3.42 (3.35)	25.79 (25.88)	21.73 (21.93)	0.77	1.91	1.04

[a] HAd = 6-aminopurine (adenine).
[b] Isomer shift with respect to the centroid of a room temperature $BaSnO_3$ spectrum.
[c] Nuclear quadrupole splitting.
[d] Full width at half height of the resonant peaks, average.

p.q.s. value around zero (+ 0.002) has been obtained from Eq. (2) for ([N] – [hal])$_{oct}$ (*i.e.*, for the contribution of Ad/2 to the e.f.g.); this figure fits reasonably well, *inter alia*, to p.q.s.$_{oct}$ of dinitrogen chelating ligands such as bipyridyl and *o*-phenanthroline,[4,5] as well as to p.q.s.([Ox/2] – [hal])$_{oct}$ = –0.05 mm s^{-1} calculated with Eq. (2) for bis(8-oxyquinolinato)diorganitin(IV), all considered to assume a *cis*-R_2 octahedral configuration (exptl. ΔE taken from literature, see ref. 3a). It follows that a *cis*-R_2 octahedral arrangement, as in Fig. 1b, cannot be *a priori* excluded for R_2SnAd_2 on the basis of Mössbauer spectroscopic data. Anyhow, it seems quite unlikely to assume a chelating behaviour of the adeninato(1–) anion through N^9, N^3 atoms in these complexes; in fact, adenine or adeninato(1–) act as bridging bis-monodentate ligands when coordinating through both N^9 and N^3, as in $[Cu_2(HAd)_4(H_2O)_2]^{4+}$ and related species,[8] and chelation by N^9, N^3 apparently was never detected. A bridging behaviour of the above mentioned type would then be eventually surmised for adeninato(1–) with formation of dimers $(R_2SnAd_2)_2$, with a *cis*-R_2 octahedral environment (very probably distorted) around Sn^{IV}.

Further work is in progress in order to determine the actual configuration of R_2SnAd_2, and studies are under way on R_nSn^{IV} derivatives of adenosine and AMP.

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References

1 L. Pellerito, M. T. Lo Guidice, G. Ruisi, N. Bertazzi, R. Barbieri and F. Huber, *Inorg. Chim. Acta*, (1975) to be published.
2 R. Barbieri, G. Alonzo, A. Silvestri, N. Burriesci, N. Bertazzi, G. C. Stocco and L. Pellerito, *Gazz. Chim. Ital.*, *104*, 885 (1974).
3 a) Data reported by P. J. Smith, *Organometal. Chem. Rev. A*, *5*, 373 (1970); b) P. J. Smith, R. F. M. White and L. Smith, *J. Organometal. Chem.*, *40*, 341 (1972).
4 See for example: a) G. M. Bancroft and R. H. Platt, *Adv. Inorg. Chem. Radiochem.*, *15*, 59 (1972); b) R. V. Parish, *Progress Inorg. Chem.*, *15*, 101 (1972).
5 M. G. Clark, A. G. Maddock and R. H. Platt, *J. Chem. Soc. Dalton*, 281 (1972).
6 P. de Meester and A. C. Skapski, *J. Chem. Soc. Dalton*, 424 (1973); *id.*, *ibid.*, 1596 (1973); T. J. Kistenmacher, *Acta Cryst.*, *B30*, 1610 (1974).
7 G. L. Eichhorn, "Complexes of Nucleosides and Nucleotides", in "Inorganic Biochemistry", G. L. Eichhorn Ed., Elsevier, Amsterdam (1973) Ch. 33.
8 A. Terzis, A. L. Beauchamp and R. Rivest, *Inorg. Chem.*, *12*, 1166 (1973) and refs. therein.