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6-Thiopurine Complexes of Organotin(IV) Moieties. Synthesis and Structural Characterization by Infrared and Mössbauer Spectroscopy

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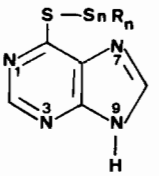
The novel complexes $Me_3Sn(6\text{-}TP^{-1})$ and $Bu^n_2Sn(6\text{-}TP^{-1})_2$, where $6\text{-}TP^{-1}$ is the mono-anion of 6-thiopurine, have been synthesized. The sites of stannylation of 6-TP have been inferred from the known directions of electrophilic substitution reactions of 6-TP itself. The compounds have been characterized by infrared and Mössbauer spectroscopy. A solid state polymeric structure has been proposed for $Me_3Sn(6\text{-}TP^{-1})$, where planar SnC_3 skeletons are bridged by $6\text{-}TP^{-1}$ (thione tautomer) axially bound to Sn through N(3) and N(1) atoms. For $Bu^n_2Sn(6\text{-}TP^{-1})_2$, a molecular structure has been advanced, with the 'aromatic' ligand anions chelating Sn by S-N(7) atoms.

Introduction

6-thiopurine (6-TP) is an anticancer antimetabolite (*inter alia*), clinically effective against human leukemias [1]. Its complexes with platinum, palladium and bismuth exhibit antitumor activity too, activity which in some cases is enhanced with respect to that of 6-TP itself [2]. It has been recently observed that several diorganotin(IV) compounds, some R_2SnX_2 six-coordinate adducts with pyridine, o-phenanthroline and 2,2'-bipyridyl, and R_2Sn^{IV} complexes with adenine and glycylglycine, are effective antineoplastic (mainly antileukemic) agents [3]. The complexation of organotin(IV) moieties by 6-TP could then in principle yield a synergistic therapeutic effect. We planned a research work in this field, and report in this paper some preliminary results on the synthesis and structural spectroscopic (infrared and Mössbauer) characterization, of two novel 6-TP derivatives of organotin(IV). The evaluation of their antitumor activity is currently underway.

Discussion

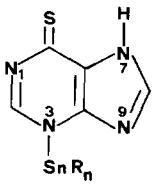
It has been reported that the reaction of 6-TP and of 6-methylthiopurine with hexaphenyldistannoxane in boiling acetone affords products with the unexpected stoichiometries Ph_3Sn^{IV}: 6-TP = 3:2 and 1:2, respectively [4]. We tried two synthetic routes: i) reaction of R_3SnOH with 6-TP (1:1) in hot acetone, analogously to [4], and ii) reaction in hot methanol of R_2Snhal_2 with $6\text{-}TP^{-1}$ (1:2), the latter obtained by deprotonation of 6-TP by methoxide. Till now $Me_3Sn(6\text{-}TP^{-1})$ has been synthesized by method i), and $Bu^n_2Sn(6\text{-}TP^{-1})_2$ by method ii) (see Experimental). Information on the configuration of the latter products may be first gained through the discussion of the pathways of the synthetic processes. The procedure under i) consists of a substitution reaction, presumably heterolytic, with the electrophilic attack of the oxygen atom by a proton of 6-TP, as well as of $6\text{-}TP^{-1}$ by R_3Sn^+ [5]. In ii), $6\text{-}TP^{-1}$ is electrophilically attacked by R_2Sn^{2+} (or R_2Snhal^+). Mono-deprotonation of 6-TP would take place at N(1) [6, 7], the negative charge residing on the sulfur atom of the resulting 'aromatic' tautomer [6]. It must be also recalled that methylation of 6-TP yields initially 6-methylthiopurine [8a], which essentially assumes the N(9)H 'aromatic' tautomeric form both in solution and in the solid [9, 10]. As a consequence, it could be expected that, by reactions i) and ii), S-stannylation of 6-TP primarily occurs, yielding tautomers of type (I), where one and two $6\text{-}TP^{-1}$ are bound to R_nSn^{IV} for n = 3 and = 2 respectively.



(I)

At high temperature (≥40 °C), 6-methylthiopurine suffers N(3)-methylation and S-demethylation, the thione group being restored [8a]. An analogous process could in principle occur also for our stannyl

derivatives, due to the high temperature of the reaction mixture in i) and ii) (refluxing solvent), yielding tautomer (II).



(II)

From the directions of the electrophilic substitution reactions of 6-TP, it is then predicted that the possible sites of primary attack of 6-TP by R_nSn^{IV} moieties are the S and N(3) atoms.

Further configurational information is obtained by the spectroscopic characterization of the solids. From the infrared data of Table I, it would appear that the intermolecular N–H---N bonds present in 6-TP are preserved in our complexes. For $Bu^n_2Sn(6\text{-}TP^{-1})_2$, the ν(N–H---N) band [8b, 11] corresponds to that observed in several other adducts and complexes of 6-TP [11, 12], while appearing less intense in $Me_3Sn(6\text{-}TP^{-1})$. This is at variance with the data reported for the Ph_3Sn^{IV} derivatives, where this absorption is lacking [4]. The purine ring skeletal vibrations [8b, 13, 14] essentially correspond in 6-TP and its complexes (Table I), which suggests in the latter the occurrence of N-to-Sn coordination. In fact, the highest energy skeletal mode occurs at 1583 cm^{-1} in $6\text{-}TP^{-1}$ [15], deprotonated at N(1) [6, 7], and shifts to 1613 cm^{-1} [12, 15] in purine-6-thione, which is the 6-TP tautomer present in the solid state, with N(1)–H and N(7)–H bonds [16].

The thione group is preserved in $6\text{-}TP^{-1}$ when coordinated to Me_3Sn^{IV}, as suggested by the probable occurrence of the ν(C=S) mode, Table I [11–13], while it is lacking in $Bu^n_2Sn(6\text{-}TP^{-1})_2$, where bands around 1160–1130 cm^{-1} are undoubtedly attributable to vibrations of (Sn)Bu^n groups [17]. Absorptions related to Sn–S bonds are certainly absent in the Me_3Sn^{IV} complex and present in the $Bu^n_2Sn^{IV}$ derivative (Table I). The latter attributions are particularly reliable, since the zone 300–400 cm^{-1}, where ν(SnS) modes have been detected for a number of organotin(IV)–sulfur derivatives [18], is practically free of vibrational bands of 6-TP as well as of Me_3Sn^{IV} and $Bu^n_2Sn^{IV}$ moieties [17, 19, 20, and measurements by the authors of this paper). If a single ν(SnS) mode really occurred for $Bu^n_2Sn(6\text{-}TP^{-1})_2$ (Table I), it could be $\nu_{as}(SnS_2)$, and the S–Sn–S skeleton would be linear. In fact, both $\nu_{as}(SnS_2)$ and $\nu_s(SnS_2)$ have been detected in the tetrahedral species $Ph_2Sn(SPh)_2$ [18b]. Lastly, the existence of only $\nu_{as}(SnC_3)$ [19] in the Me_3Sn^{IV} complex (Table I) implies the planarity of the SnC_3 skeleton. No configurational information may be extracted from $\nu(SnC_2)$ modes in $Bu^n_2Sn^{IV}$ derivatives [17, 20].

TABLE I. Some Relevant Infrared Absorptions[a], and Mössbauer Parameters.

Compound[b]	H-bonded ν(NH)[c]	Purine ring skeletal vibrations	ν(C=S)	$\nu(SnC_n)$	ν(SnS)	δ[g]	ΔE_{exp}[h]	ΔE_{calcd}[i] (structure)
$Me_3Sn(6\text{-}TP^{-1})$	3100–2200 s, bd	1590 vs, bd; 1520 s	1135 mw	535 vs[d]	–	1.351 (±0.006)	3.217 (±0.003)	−3.250 (III)
$Bu^n_2Sn(6\text{-}TP^{-1})_2$	3600–2200 s, bd	1605 s; 1585 sh; 1565 m; 1545 m; 1520 m	–	605 vs[e] 525 w[e]	305 ms[f]	1.546 (±0.011)	3.257 (±0.043)	−3.431 (IV)
6-TP(anhydrous)	3300–2200 s, bd	1610 s, bd; 1570 s; 1555 s; 1530 m; 1500 mw	1155 m					

[a] Wavenumbers, cm^{-1}. s = strong, m = medium, w = weak, bd = broad, sh = shoulder, v = very. The band assignments are commented also in the text. [b] 6-TP is 6-thiopurine (purine-6-thione). [c] Complex structure. Includes ν(CH). See text for Refs. [d] $\nu_{as}(SnC_3)$ [19]. No band attributable to $\nu_s(SnC_3)$ has been detected. [e] Tentative assignments to $\nu_{as} + \nu_s(SnC_2)$ II and I, respectively [17]. Contributions by ligand vibrations are possible. [f] Probably $\nu_{as}(SnS_2)$ [18b]. [g] Mössbauer isomer shift at 77.3 K with respect to R.T. $CaSnO_3$, mm s^{-1}, average (standard error). [h] Experimental nuclear quadrupole splitting at 77.3 K, mm s^{-1}, average (standard error). Full widths at half height of the resonant peaks are 0.85÷0.90 mm s^{-1} for absorber thicknesses 0.50÷0.58 mg $^{119}Sn/cm^2$. [i] Point-charge model estimates of the quadrupole splitting for tin environments (III) and (IV), Fig. 1. Partial quadrupole splittings, p.q.s., employed in the calculations are literature values [21]. In particular, the p.q.s. $\{N\}^{tba}$ = −0.035 mm s^{-1} has been used for (III) (*i.e.*, the value for trigonal bipyramidal axial pyridine); besides, for (IV) the p.q.s. $([N]-[hal])^{oct}$ = −0.04, $([S]-[hal])^{oct}$ = −0.56, mm s^{-1}, have been employed (*i.e.*, the values for *o*-phenanthroline and ethanedithiolate in octahedral structures, respectively).

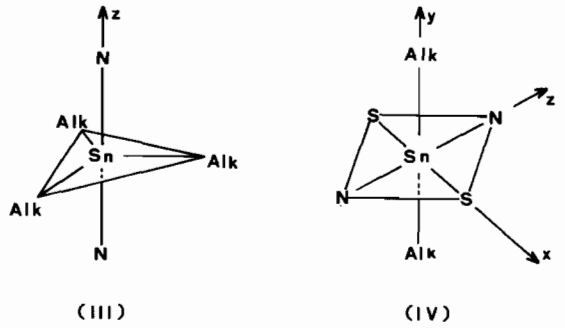


Fig. 1. The environments of tin in $Me_3Sn(6\text{-}TP^{-1})$ (III) and $Bu^n_2Sn(6\text{-}TP^{-1})_2$ (IV) according to the point-charge model rationalization of the Mössbauer quadrupole splittings ΔE (see Table I and text). The directions of the principal components of the electric field gradient tensor, $V_{\alpha\alpha}$ [21], are shown. The calculated asymmetry parameters [21] are η = 0.00 (III) ($V_{xx} = V_{yy}$) and η = 0.93 (IV).

The environment of tin in the 6-TP complexes has been further investigated by Mössbauer spectroscopy. The magnitude of the parameters isomer shift, δ (Table I), is typically in the range of Alk_3Sn^{IV} and Alk_2Sn^{IV} derivatives [21]. The experimental nuclear quadrupole splittings, ΔE_{exp}, agree perfectly with values calculated by the point-charge model formalism [21], ΔE_{calcd} (Table I), for a trigonal bipyramidal distribution of charge density at tin in $Me_3Sn(6\text{-}TP^{-1})$, (III), and for an octahedral one in $Bu^n_2Sn(6\text{-}TP^{-1})_2$, (IV). All other potentially possible five-coordinate structures, tested for the Me_3Sn^{IV} complex (*i.e.*, with facial and meridional SnC_3 skeletons, *cis*-N,N and -S,N, as well as equatorial SnC_3 and axial S,N [22]), generally yield ΔE_{calcd} values differing from ΔE_{exp} by more than the limiting accepted value 0.4 mm s^{-1} [23], with the exception of the isomer with meridional SnC_3 and equatorial S and N (ΔE_{calcd} = −2.906). This, on the other hand, must be excluded in view of the absence of Sn–S bonds determined by the infrared study. Four-coordinated, tetrahedral type structures Me_3Sn–S– and Me_3Sn–N< are ruled out too, their ΔE_{exp} being expected around 2 and 1 mm s^{-1} respectively [24, 25] (a weak Sn–N–Sn interaction, on the other hand, is assumed in the Me_3Sn^{IV} derivatives of dialkyl- and cyclic amines [25]).

As far as $Bu^n_2Sn(6\text{-}TP^{-1})_2$ is concerned, the structural isomers of (IV) with *trans*-C_2, *cis*-S_2 and -N_2(ΔE_{calcd} = +2.920), and *cis*-C_2 and -S_2, *trans*-N_2 (ΔE_{calcd} = −3.020), could also be assumed on the basis of the point-charge model treatment of ΔE. On the other hand, *cis*-S_2 configurations would be ruled out by the occurrence of only $\nu_{as}(SnS_2)$ in the infrared (*vide supra*). Five-coordinated structures (equatorial C_2) are excluded, except C_2SnN_3 with a meridional SnN_3 skeleton (ΔE_{calcd} = +2.964), and C_2SnSN_2 with axial N_2 and equatorial S (ΔE_{calcd} = −2.871); the latter two configurations are in turn largely improbable due to the inconsistency with infrared data (C_2SnN_3) and to the high difference $\Delta E_{exp} - \Delta E_{calcd}$ (=0.39 for C_2SnSN_2). Lastly, the four-coordinated species $Bu^n_2Sn(S\text{-}R)_2$ is ruled out since its ΔE_{exp} is expected to be about 2 mm s^{-1} (1.96 for $Bu^n_2Sn(SPh)_2$ [26]).

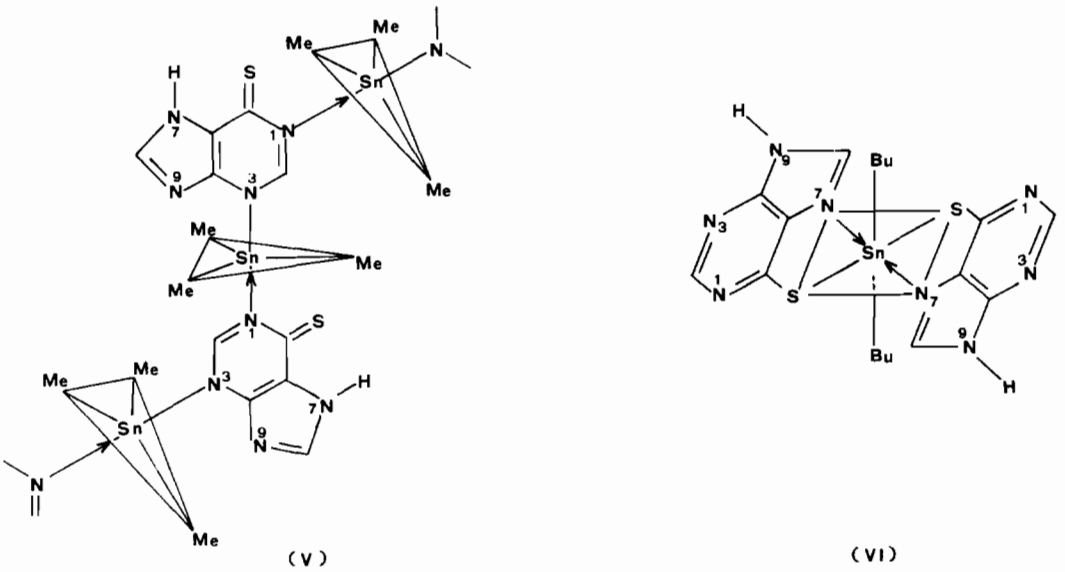
Quite different structures for our compounds then emerge from the spectroscopic studies. The Me_3Sn^{IV} complex seems a solid state polymer where the environment of tin is of type (III), while the $Bu^n_2Sn^{IV}$ derivative is very probably a molecular solid, as (IV), with $6\text{-}TP^{-1}$ chelating Sn through S–N(7) atoms. Two questions now arise: i) which nitrogen atoms of the purine ring are bound to Sn in the Me_3Sn^{IV} complex?, and ii) what are the reasons for the structural characteristics of our compounds?

Owing to the absence of Sn–S bonds, it appears that the stannylation of 6-TP by Me_3Sn^{IV} has been directed to the N(3) site yielding the tautomer (II), as discussed in the preceding. Taking now into account [7] that protonation of 3-methyl-6-thiopurine occurs at N(1), a further intermolecular coordination of tin by N(1) atoms may be advanced in solid $Me_3Sn(6\text{-}TP^{-1})$, thus attaining a polymeric trigonal bipyramidal structure, quite common in R_3Sn^{IV} derivatives. This assumption is in some way confirmed by the Mössbauer ΔE values reported for the solid state polymers Alk_3 Sn-imidazole, -2-Me-imidazole and -benzimidazole, where planar SnC_3 skeletons are intermolecularly bridged by heterocyclic nitrogen atoms [27, 28]. These ΔE's are spread out in the range 2.76–3.65 mm s^{-1} and their average ΔE_{av} = 3.11 mm s^{-1} [28] corresponds to the Me_3Sn-($6\text{-}TP^{-1}$) value (Table I).

It must be recalled that the only other R_3Sn^{IV} derivative of a 6-TP analogue so far reported and spectroscopically characterized is the $Bu^n_3Sn^{IV}$ complex of 2′, 3′-isopropylidene-6-thiopurine riboside, where chelation of tin by S–N(7) atoms has been assumed [29]. Primary S-stannylation in this compound is consistent with the reaction conditions (ligand + $(Bu_3Sn)_2O$ in $CHCl_3$ at room temperature [29]), although the apparent lack of N(3) stannylation could be due to steric hindrance by the N(9)-bonded ribofuranose residue.

As far as $Bu^n_2Sn(6\text{-}TP^{-1})_2$ is concerned, the S-stannyl tautomer (I) would be obtained and stabilized by chelation of tin through coordination of the N(7) atoms, thus yielding an octahedral type structure commonly occurring in R_2Sn^{IV} complexes. Chelated S–N(7) 6-TP has been detected by X-ray diffractometry in a number of transition metal ion derivatives [30].

The structures (V) and (VI) then definitely emerge from the present investigation for $Me_3Sn(6\text{-}TP^{-1})$ and $Bu^n_2Sn(6\text{-}TP^{-1})_2$ respectively. In particular, no steric constraints to the formation of intermolecular



(V) (VI)

Fig. 2. The structures proposed for solid $Me_3Sn(6\text{-}TP^{-1})$ (V) and $Bu^n_2Sn(6\text{-}TP^{-1})_2$ (VI) according to infrared and Mössbauer spectroscopic data, as well as to the possible stannylation sites of 6-TP.

N–H---N bonds (detected in the infrared spectra, *vide supra*) appear in (V) and (VI), which are then fully consistent with all experimental evidence discussed in the preceding.

The work presently in progress is devoted to a better understanding of the pathways of the reactions of tin(IV) and organotin(IV) derivatives with 6-TP, and of the correlation of the experimental conditions with the structure of the products. For example, evidence has been already obtained that temperature plays a definite role, analogous to that in the methylation of 6-TP commented in the preceding. In fact, Ph_3SnOH has been repeatedly reacted with equimolar amounts of 6-TP (method i), under reflux (as in Ref. [4]) as well as at room temperature, generally obtaining products with apparent 1:1 composition. The Mössbauer spectra of the solid samples coming from the high temperature syntheses show four resonant lines suggesting the occurrence of two different tin sites, while apparently two line spectra, with large values of full width at half height, are detected for samples prepared at room temperature.

Experimental

Organotin(IV) compounds were a gift from Schering A.G., Bergkamen (B.R.D.), and 6-TP·H_2O was a Fluka product.

The syntheses were effected by the following procedures:

$Me_3Sn(6\text{-}TP^{-1})$, method i): 5 mmol of both Me_3SnOH and 6-thiopurine hydrate were refluxed (~1 hour) in 100 ml of acetone, causing the formation of a clear solution. The volume of the reaction mixture was then reduced to 50 ml by distillation of the solvent, when a white microcrystalline precipitate was obtained. This was filtered off, washed with acetone and dried under vacuum. M.p. (uncorrected) 208–209 °C. Analytical %, calculated for $C_8H_{12}N_4SSn$: C, 30.51; H, 3.84; N, 17.79; Sn, 37.68. Found: C, 30.64; H, 3.62; N, 17.58; Sn, 37.32.

$Bu^n_2Sn(6\text{-}TP^{-1})_2$, method ii): 6-thiopurine was dehydrated by heating at 150 °C for 24 hours. 4 mmol of the ligand were then mono-deprotonated by reaction with the equimolar amount of CH_3ONa in 50 ml of anhydrous CH_3OH, and the resulting solution added to 2 mmol of $Bu^n_2SnCl_2$ in 10 ml of anhydrous CH_3OH. The reaction mixture was refluxed with stirring for about 4 hours, then evaporated to about 20 ml, and the precipitated NaCl filtered off. The solution was added to ethyl ether, the eventually-formed NaCl filtered, and the clear solution kept at about −10 °C for one week. Pale yellow crystals were obtained, which were filtered off, washed, and dried under vacuum. M.p. (unc.) 265–268 °C. Analytical %, calculated for $C_{18}H_{24}N_8S_2Sn$: C, 40.39; H, 4.52; N, 20.93; Sn, 22.17. Found: C, 40.27; H, 4.52; N, 20.87; Sn, 22.58.

The infrared spectra were measured by a Perkin-Elmer Mod. 580 instrument, on nujol and hexachlorobutadiene mulls between CsI discs. The Mössbauer spectra were determined at 77.3 K by the usual apparatus, techniques and procedures for computer reduction of data [31]. In particular, the source (10 mCi, $Ca^{119}SnO_3$ from R.C., Amersham) was moving at room temperature with constant

acceleration in a triangular waveform. Infrared and Mössbauer spectra were repeatedly taken on samples of our complexes coming from at least three distinct synthetic batches for each product, as well as on samples recrystallized from hot methanol or ethanol, obtaining reproducible infrared frequencies and Mössbauer parameters (reported in Table I).

The calculation of point-charge model values of Mössbauer quadrupole splittings, ΔE, was carried out by the aid of a computer program which diagonalizes the electric field gradient (EFG) tensor for any given assigned structure and assumed set of partial quadrupole splitting input data, then giving the directions of the principal components of the EFG tensor, and the sign and value of ΔE, as well as the value of the asymmetry parameter

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}}$$

[21]. The program was written by T. C. Gibb (Leeds).

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References

1 P. Calabresi and R. E. Parks, Jr., 'Alkylating Agents, Antimetabolites, Hormones and other Antiproliferative Agents', in 'The Pharmacological Basis of Therapeutics', L. S. Goodman and A. Gilman (eds.), Mac Millan, N.Y. (1975); ch. 62.
2 S. Kirshner, Y. K. Wei, D. Francis and J. G. Bergman, *J. Medicinal Chem., 9,* 369 (1966); S. M. Skinner and R. W. Lewis, *Res. Communs. Chem. Pathol. Pharmacol., 16,* 183 (1977); S. M. Skinner, J. M. Swatzell and R. W. Lewis, *ibid., 19,* 165 (1978); M. Das and S. E. Livingstone, *Br. J. Cancer, 38,* 325 (1978).
3 A. J. Crowe and P. J. Smith, *Chem. Ind. (London),* 200 (1980); A. J. Crowe, P. J. Smith and G. Atassi, *Chem.-Biol. Interact., 32,* 171 (1980); E. J. Bulten, Org. Chem. Inst. TNO, Utrecht, Holland, private communication; Natl. Cancer Inst., Div. of Cancer Treatment, Bethesda, Md., U.S.A., private communication; R. Barbieri, L. Pellerito, G. Ruisi, M. T. Lo Giudice, F. Huber and G. Atassi to be published.
4 E. J. Kupchik and E. F. McInerney, *J. Organometal. Chem., 11,* 291 (1968).
5 A. J. Bloodworth and A. G. Davies, 'Organotin Compounds with Sn–O Bonds—Organotin Alkoxides, Oxides, and Related Compounds', in 'Organotin Compounds', A. K. Sawyer Ed., M. Dekker, N.Y. (1971), Vol. 1, ch. 4, p. 153.
6 F. Bergmann, M. Kleiner, Z. Neiman and M. Rashi, *Israel J. Chem., 2,* 185 (1964).
7 D. Lichtenberg, F. Bermann and Z. Neiman, *Israel J. Chem., 10,* 805 (1972).
8 J. H. Lister, R. L. Jones, P. D. Lawley, G. H. Hitchings and G. B. Elion, 'Fused Pyrimidines—Part II, Purines', D. J. Brown (ed.), in 'The Chemistry of Heterocyclic Compounds', A. Weissberger and E. C. Taylor (eds.), Wiley–Interscience, N.Y. (1971). a) ch. VII, p. 269. b) ch. XIII, p. 496.
9 U. Reichman, F. Bergmann, D. Lichtenberg and Z. Neiman, *J. Chem. Soc. Perkin I,* 793 (1973).
10 W. J. Cook and C. E. Bugg, *J. Pharm. Sciences, 64,* 221 (1975).
11 H. Hadjiliadis and T. Theophanides, *Canad. J. Spectrosc., 22,* 51 (1977), and Refs. therein.
12 N. Kottmair and W. Beck, *Inorg. Chim. Acta, 34,* 137 (1979).
13 E. Spinner, *J. Chem. Soc.,* 1237 (1960), and Refs. therein.
14 D. Garfinkel and J. T. Edsall, *J. Amer. Chem. Soc., 80,* 3807 (1958).
15 W. Beck and N. Kottmayr, *Chem. Ber., 109,* 970 (1976).
16 E. Sletten, J. Sletten and L. M. Jensen, *Acta Cryst., B25,* 1330 (1969); G. M. Brown, *ibid.,* 1338.
17 H. Geissler and H. Kriegsmann, *J. Organometal. Chem., 11,* 85 (1968).
18 a) R. C. Poller and J. A. Spillman, *J. Chem. Soc. (A),* 958 and 1024 (1966); b) H. Schumann and P. Reich, *Z. Anorg. allg. Chem., 375,* 72 (1970); c) T. A. George, *J. Organometal. Chem., 31,* 233 (1971); d) J. R. May, W. R. Mc Whinnie and R. C. Poller, *Spectrochim. Acta, 27A,* 969 (1971).
19 W. F. Edgell and C. H. Ward, *J. Molecular Spectroscopy, 8,* 343 (1962).
20 M. C. Tobin, *J. Molecular Spectroscopy, 5,* 65 (1960).
21 G. M. Bancroft and R. H. Platt, *Adv. Inorg. Chem. Radiochem., 15,* 59 (1972), and Refs. therein; G. M. Bancroft, V. G. Kumar Das, T. K. Sham and M. G. Clark, *J. Chem. Soc. Dalton,* 643 (1976).
22 In addition to partial quadrupole splittings quoted in Refs. [21], and in footnote (h) to Table I of this paper, the following trigonal bipyramidal p.q.s. s have been employed in the point-charge model calculations: $\{N\}^{tbe}$ = $\{py\}^{tbe}$ = +0.147 (from $\{py\}^{tba}$, Ref. [21]); $\{S\}^{tba}$ = −0.595; $\{S\}^{tbe}$ = −0.60, mm s^{-1}, the latter two being unpublished data from the present Authors.
23 M. G. Clark, A. G. Maddock and R. H. Platt, *J. Chem. Soc. Dalton,* 281 (1972).
24 P. L. Clarke, R. A. Howie and J. L. Wardell, *J. Inorg. Nuclear Chem., 36,* 2449 (1974).
25 M. E. Bishop and J. J. Zuckerman, *Inorg. Chem., 16,* 1749 (1977).
26 R. C. Poller and J. N. R. Ruddick, *J. Organometal. Chem., 60,* 87 (1973).
27 J. G. A. Luijten, M. J. Janssen and G. J. M. van der Kerk, *Rec. Trav. Chim. Pays Bas, 81,* 202 (1962); M. J. Janssen, J. G. A. Luijten and G. J. M. van der Kerk, *J. Organometal. Chem., 1,* 286 (1964).
28 R. H. Herber, H. A. Stockler and W. T. Reichle, *J. Chem. Phys., 42,* 2447 (1965); R. V. Parish and R. H. Platt, *J. Chem. Soc. (A),* 2145 (1969); R. Gassend, J. C. Maire and J. C. Pommier, *J. Organometal. Chem., 132,* 69 (1977).
29 G. Domazetis, R. J. Magee and B. D. James, *J. Organometal. Chem., 197,* 39 (1980).
30 D. J. Hodgson, *Progress Inorg. Chem., 23,* 211 (1977), and Refs. therein; E. A. H. Griffith and E. L. Amma, *J. Chem. Soc. Chem. Comm.,* 1013 (1979).
31 R. Barbieri, G. Alonzo, A. Silvestri, N. Burriesci, N. Bertazzi, G. C. Stocco and L. Pellerito, *Gazz. Chim. Ital., 104,* 885 (1974).