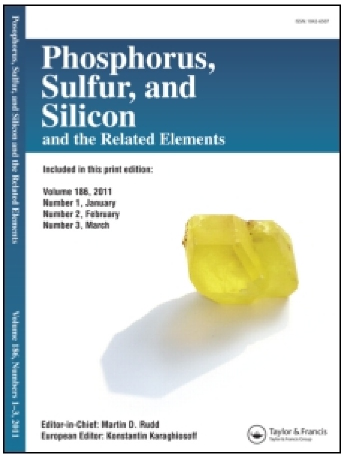

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STUDIES ON BINUCLEAR COMPLEXES DERIVED FROM SULFUR CONTAINING ORGANIC MOIETIES

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STUDIES ON BINUCLEAR COMPLEXES DERIVED FROM SULFUR CONTAINING ORGANIC MOIETIES

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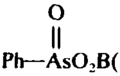
Synthetic, spectroscopic and biological features of some binuclear complexes with monofunctional bidentate heterocyclic thiosemicarbazones have been described. The resulting derivatives of the type,  $\mathrm{Ph{-}\overset{\overset{O}{\|}}{As}O_2B(TSCZ)}$ (where TSCZ ^{1} represents the anion of thiosemicarbazone moiety) are colored solids and non-electrolytic in nature. On the basis of analytical data, IR, ^{1}H, ^{13}C and ^{11}B NMR spectral studies, a tri-coordinated environment for boron and a penta-coordinated environment around arsenic may be assigned to the resulting binuclear complexes. Some representative ligands as well as their binuclear complexes have also been evaluated for their antifungal and antibacterial activities.

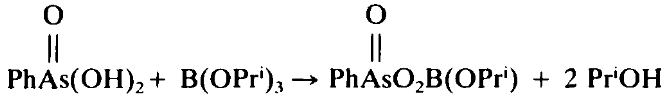
Key words: Heterocyclic thiosemicarbazones; synthesis, spectral and biological studies.

INTRODUCTION

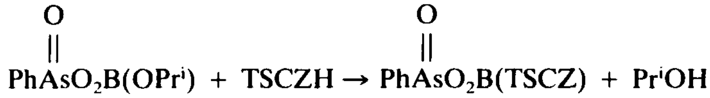
An intensive scrutiny of the literature reveals that there is an interest in undertaking systematic studies on N and O/S donor systems on account of their biochemical significance[1–4] in different aspects of human environment. These ligands, depending upon the reaction conditions, may act as ionic or neutral[5] moieties having interesting stereochemistry, as only the β-nitrogen coordinates[6] to the metal atom, while the α-nitrogen remains uncoordinated. The remaining oxygen or sulfur has a tendency to form strong covalent bond with the metal atom. Synthetic studies have been previously carried out on transition metal complexes[7–10] with a variety of azomethine ligands having N and O/S as donors. In view of the versatile chelating ability, widespread applications and much data involving organometallic derivatives of both arsenic and boron in one complex, it has been considered worthwhile to examine the reaction of $PhAsO_3H_2$ and $B(OPr^i)_3$ with thiosemicarbazones derived from heterocyclic aldehydes and ketones.

RESULTS AND DISCUSSION

The reactions of phenylarsonic acid with triisopropoxy borane and monobasic bidentate, thiosemicarbazones having NS donor system in 1:1:1 molar ratio have been carried out in dry benzene and these may be depicted by the following equations:



$$\mathrm{Ph\overset{\overset{O}{\|}}{As}(OH)_2 + B(OPr^i)_3 \rightarrow Ph\overset{\overset{O}{\|}}{As}O_2B(OPr^i) + 2\ Pr^iOH}$$



$$\mathrm{Ph\overset{\overset{O}{\|}}{As}O_2B(OPr^i) + TSCZH \rightarrow Ph\overset{\overset{O}{\|}}{As}O_2B(TSCZ) + Pr^iOH}$$

(where TSCZH denotes the thiosemicarbazone moiety).

These reactions proceed smoothly with the formation of isopropanol which is removed azeotropically with benzene. All the newly synthesized complexes have been isolated as colored solids and these are soluble in DMSO, THF, DMF and benzene. Molecular weight determinations have shown the monomeric nature of these complexes and the non-electrolytic behaviour of the complexes in Dry DMF is indicated by low value (10–15 $\mathrm{ohm^{-1}cm^2mol^{-1}}$) of molar conductance.

SPECTRAL STUDIES

IR Spectra

In the IR spectra of thiosemicarbazones, a broad absorption band in the region, 3300–3100 $\mathrm{cm^{-1}}$ has been assigned to ν(NH) vibrations. Similarly, in phenylarsonic acid, the absorption band in the region, 2700–2300 $\mathrm{cm^{-1}}$ is due to ν(OH) of phenyl arsonic acid. In the binuclear complexes these bands are found to be absent indicating the deprotonation of these groups and subsequent bonding of boron with sulfur attached to the carbon atom adjacent to the NH group as well as with both the oxygens of OH groups of phenylarsonic acid.

The formation of boron-oxygen and boron-sulfur bonds is also supported by the appearance of new bands at ca. 1350 and 860 $\mathrm{cm^{-1}}$ assignable to $\nu(\mathrm{B{-}O})$ and $\nu(\mathrm{B{-}S})$[11] vibrations, respectively. The bands attributable to symmetric and asymmetric modes of vibrations of $\mathrm{As}\begin{smallmatrix}\diagup \mathrm{O}\\ \diagdown \mathrm{O}\end{smallmatrix}$ group are observed at ca. 760 and 830 $\mathrm{cm^{-1}}$, respectively.[16] A strong band in the complexes at ca. 980 $\mathrm{cm^{-1}}$ may be assigned to the stretching frequency of the free $\mathrm{As{=}O}$ group.[13]

All the ligands exhibit a strong band at ca. 1605 ± 10 $\mathrm{cm^{-1}}$ due to the $\nu(\mathrm{>C{=}N})$ stretching vibrations[14] and this is shifted towards the higher frequency side due to the coordination of the azomethine nitrogen to the boron atom. This is further supported by the appearance of a new band at ca. 1540 $\mathrm{cm^{-1}}$ due to $\nu(\mathrm{B \leftarrow N})$[15] in the spectra of complexes.

PMR Spectra

The PMR chemical shift data of ligands Fur.TSCZH and Thiop.TSCZH along with their corresponding binuclear oxobridged complexes have been scanned in $\mathrm{DMSO{-}d_6}$ and the relevant data are compiled in Table I.

TABLE I

^1H NMR Spectral data (δ, ppm) of ligands and their corresponding binuclear complexes

Compound	-NH	$-NH_2$	$-\underset{\substack{\vert\\ \mathrm{H}}}{\mathrm{C}}=\mathrm{N}$	Aromatic
Fur.TsczH	10.74	2.83	8.68	8.06-6.85
$PhAsO_3B$(Fur.Tscz)	-	2.86	8.85	8.53-7.02
Pyd.TsczH	10.91	2.86	8.72	8.58-7.29
$PhAsO_3B$(Thiop.Tscz)	-	2.89	8.87	8.70-7.36

TABLE II

Binuclear As-O-B type of complexes of monofunctional bidentate thiosemicarbazones derived from heterocylic aldehyde and ketones

Reactants			Product formed and colour	M.P. (°C)	Yield (%)	Elemental analyses (%)				Mol.Wt.
Pheynyl-arsonic acid(g)	$B(OPr^i)_3$ (g)	Ligand (g)				N Found (Calcd)	S Found (Calcd)	B Found (Calcd.)	As Found (Calcd)	Found (Calcd.)
0.78	0.72	$C_6H_7N_3SO$ 0.65	$C_{12}H_{11}N_3SO_4BAs$ Orange red	242	78	11.28 (11.09)	8.25 (8.46)	2.67 (2.85)	20.03 (19.77)	394.38 (379.00)
0.98	0.92	$C_6H_7N_3S_2$ 0.90	$C_{12}H_{11}N_3SO_3BAs$ Brick red	182	85	10.47 (10.64)	16.07 (16.23)	2.48 (2.74)	19.18 (18.96)	416.12 (395.10)
0.71	0.66	$C_7H_9N_4S$ 0.63	$C_{13}H_{12}N_4SO_3BAs$ Orange	264	80	14.70 (14.36)	8.04 (8.22)	2.68 (2.77)	19.45 (19.20)	368.47 (390.05)
0.97	0.90	$C_{10}H_{10}N_4S$ 1.04	$C_{16}H_{14}N_4SBAs$ Yellowish	290(d)	83	13.32 (13.08)	7.21 (7.49)	2.41 (2.52)	17.26 (17.50)	405.11 (428.10)
0.89	0.83	$C_7H_9N_3SO$ 0.81	$C_{13}H_{13}N_3SO_4BAs$ Dark Brown	196	76	10.38 (10.69)	8.40 (8.16)	2.44 (2.75)	19.28 (19.06)	415.52 (393.06)
0.89	0.83	$C_7H_9N_3S_2$ 0.88	$C_{13}H_{13}N_3S_2O_2BAs$ Yellow	272	82	10.59 (10.27)	15.88 (15.67)	2.37 (2.64)	18.04 (18.31)	430.22 (409.12)
0.77	0.71	$C_8H_{10}N_4S$ 0.74	$C_{14}H_{14}N_4SO_3BAs$ Yellow	279	86	14.05 (13.86)	8.16 (7.93)	2.92 (2.67)	18.27 (18.54)	390.42 (404.08)
0.88	0.82	$C_{11}H_{12}N_4S$ 1.02	$C_{17}H_{16}N_4SO_3BAs$ Dark Yellow	320(d)	80	12.90 (12.67)	7.02 (7.25)	2.23 (2.44)	17.14 (16.94)	462.23 (442.14)

• Satisfactory C and H analyses were obtained.

The NH proton signals at δ 10.74 and 10.91 ppm in Fur.TSCZH and Thiop.TSCZH, disappear in the chelates implying the deprotonation of the NH group due to thioenolisation and involvement of sulfur in bonding with boron.

The broad singlets at ca. δ 2.83 and 2.86 ppm due to the NH_2 group remain almost unchanged in the complexes indicating that this group does not participate in complexation. However, the signal due to $-\underset{\substack{\vert\\ \mathrm{H}}}{\mathrm{C}}=\mathrm{N}$ in the free ligands (δ 8.68 and 8.72 ppm) shifted downfield in the spectra of complexes supporting the co-ordination of the azomethine nitrogen to the boron atom. The aromatic protons are observed in between δ 7.02–8.70 ppm in the complexes.

^{11}B NMR

The ^{11}B NMR spectral studies for the resulting oxo-bridged boron complexes finally confirm the tetra-coordinated state of boron. The strong intensity signal observed in the region, δ 6.50–10.60 ppm is in agreement with the reported values for the tetra-coordinated boron.[16,17]

Thus on the basis of the above spectral evidence and monomeric nature of the complexes, a tri-coordinated environment for boron and a penta-coordinated environment around arsenic may tentatively be proposed for the newly snythesized binuclear complexes.

BIOCIDAL ACTIVITY

Antifungal Activity

The fungicidal activity of some ligands and their corresponding metal chelates has been evaluated against different species of pathogenic fungi viz., *Alternaria brassicae*, *Alternaria tenuis*, *Aspergillus niger* and *fusarium oxysporum*. The fungicidal screening data of parent ligands and their complexes (Table III) indicate that the chelates are more fungitoxic than the chelating moieties themselves. This may be accounted by the chelation theory.[18]

Antibacterial Activity

The antibacterial activity of some of the complexes along with their parent ligands has been tested against *E. coli*, *Staphylococcus aureus* and *B. subtilis* (Table IV).

TABLE III

Antifungal activity of ligands and their binuclear complexes (% inhibition)

Compound	Alternaria brassicae conc. (ppm)		Alternaria tenuis conc. (ppm)		Aspergillus niger conc. (ppm)		Fusarium oxysporum conc. (ppm)	
	200	400	200	400	200	400	200	400
2-AcFur.TSCZH	24	31	21	28	32	37	22	27
2-AcThiop.TSCZH	35	39	31	38	41	47	26	34
2-AcPyd.TSCZH	30	36	29	34	37	44	23	31
$PhAsO_3B$(2-AcFur.TSCZ)	65	84	62	75	74	88	68	77
$PhAsO_3B$(2-AcThiop.TSCZ)	72	88	69	85	78	90	76	87
$PhAsO_3B$(2-AcPyd.TSCZ)	70	83	65	80	75	87	70	84

TABLE IV

Antibacterial activity of ligands and their binuclear complexes

Bacteria	Diameter of inhibition zone (mm)			
	1	2	3	4
E.coli	9	17	11	20
B.subtilis	12	21	16	25
S.aureus	10	18	13	22

1. 2-AcThiop.SCZH
2. $PhAsO_3B$(2-AcThiop.TSCZ)
3. 2-AcThiop.TSCZH
4. $PhAsO_3B$(2-AcThiop.TSCZ)

The inferences drawn from these observations clearly indicate that the ligand containing two sulfur atoms i.e. 2-AcThiop.TSCZH as well as its corresponding binuclear complex show the highest activity against all the pathogens and therefore it may be concluded that the introduction of the sulfur into an organic moiety increases its biocidal effect.[19]

EXPERIMENTAL

The reactions were carried out in Glass apparatus fitted with interchangeable joints. Extreme precautions were taken to exclude moisture throughout the experiment using $CaCl_2$ drying tubes. All the chemicals were dried and distilled before use and the reactions were carried out in a ratio head fitted with a condenser.

Preparation of Ligands. The ligands were prepared by the method reported earlier.[20] These were recrystallized and analyzed before use. Their physico-chemical properties have also been reported earlier.[20]

(i) 2-Furfuraldehyde thiosemicarbazone $C_6H_7N_3OS$ (Fur.TSCZH).
(ii) 2-Pyridinecarboxaldehyde thiosemicarbazone, $C_7H_8N_4S$ (Pyd.TSCZH).
(iii) 2-Thiophenecarboxaldehyde thiosemicarbazone, $C_6H_7N_3S_2$, (Thiop.TSCZH).
(iv) 3-Indolecarboxaldehyde thiosemicarbazone, $C_{10}H_{10}N_4S$ (3-AcIndol.TSCZH).
(v) 2-Acetylfuran thiosemicarbazone, $C_7H_9N_3SO$ (2-AcFur.TSCZH).
(vi) 2-Acetylpyridine thiosemicarbazone, $C_8H_{10}N_4S$ (2-AcPyd.TSCZH).
(vii) 2-Acetylthiophene thiosemicarbazone, $C_7H_9N_3SO$ (2-Ac-Thiop.TSCZH).
(viii) 3-Acetylindole thiosemicarbazene, $C_{11}H_{12}N_4S$ (3-AcIndol.TSCZH).

Synthesis of Complexes. The binuclear complexes were prepared by the equimolar reactions of phenylarsonic acid, boron isopropoxide and thiosemicarbazone in the medium of dry benzene in two steps. In the first step, phenylarsonic acid was reacted with an equimolar amount of boron isopropoxide and in the second step an equimolar amount of monofunctional bidentate thiosemicarbazone was added to the resulting product of the first step. The compounds were dried in vacuo. The details of these reactions and the physical properties of the compounds are recorded in Table II.

Analytical Methods and Physical Measurements. The analytical methods and procedures of physical measurements are the same as reported earlier.[20]

Biological Screening. The antifungal activity has been carried out by the radial growth method using Czapek's Agar medium[21] and the activity against bacteria was evaluated by inhibition zone technique.[21]

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REFERENCES

1. V. P. Singh, R. V. Singh and J. P. Tandon, *J. Inorg. Biochem.*, **39**, 237 (1990).
2. A. K. Saxena and F. Huber, *Coord. Chem. Rev.*, **95**, 109 (1989).
3. R. V. Singh and J. P. Tandon, *Indian J. Chem.*, **19A**, 602 (1980).
4. H. Adams, A. N. Bailey and D. E. Fenton, *J. Chem., Dalton Trans.*, **1**, 207 (1987).
5. M. Das and S. E. Livingstone, *Coord. Chem. Rev.*, **13**, 101 (1974).
6. P. K. Singh and J. P. Tandon, *J. Inorg. Nucl. Chem.*, **43**, 1755 (1981).
7. A. Garg and J. P. Tandon, *Synth. React. Inorg. Met.-Org. Chem.*, **18**, 705 (1988).
8. N. Kanoongo, R. V. Singh and J. P. Tandon, *Transition Met. Chem.*, **13**, 343 (1988).
9. N. K. Singh and R. Tripathi, *Transition Met. Chem.*, **13**, 346 (1988).
10. N. Kanoongo, R. V. Singh and J. P. Tandon, *Synth. React. Inorg. Met.-Org. Chem.*, **17**, 837 (1987).
11. L. Bhal, R. V. Singh and J. P. Tandon, *Acta Chim. Hung*, **115**, 251 (1984).
12. S. S. Sandhu, G. K. Sandhu and S. K. Pushkarna, *Synth. React. Inorg. Met.-Org. Chem.*, **11**, 197 (1981).

13. S. S. Sandhu, B. S. Manhas and H. S. Kohli, *J. Ind. Chem. Soc.*, **55,** 328 (1978).
14. V. P. Singh, R. V. Singh and J. P. Tandon, *Synth. React. Inorg. Met.-Org. Chem.*, **18,** 779 (1988).
15. K. K. Chaturvedi, R. V. Singh and J. P. Tandon, *J. Prakt. Chem.*, **324,** 817 (1984).
16. H. B. Singh and J. P. Tandon, *Synth. React. Inorg. Met.-Org. Chem.*, **15,** 391 (1985).
17. V. P. Singh, R. V. Singh and J. P. Tandon, *Nat. Acad. Sci. Letters*, **12,** 311 (1989).
18. R. S. Srivastava, *Inorg. Chim. Acta*, **56,** L65 (1981).
19. B. G. Tweedy, *Phytopathology*, **59,** 910 (1964).
20. A. Kumari, R. V. Singh and J. P. Tandon, *Main Group Met. Chem.*, **14,** 167 (1991).
21. N. Kanoongo, R. V. Singh and R. B. Goyal, *J. Inorg. Biochem.*, **38,** 57 (1990).