Inorganica Chimica Acta, 45 (1980) L231–L232
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Complexes of Dithiobenzoic Acids.
IV. Arsenic(III) Complexes

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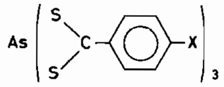
Received July 1, 1980

A number of dithiocarbamate and xanthate complexes of arsenic(III) have been prepared and particularly the former have been characterized in several ways including X-ray crystal studies [1]. However, neither the review covering these complexes [1] nor a more recent review of "dithioacid and 1,1-dithiolate complexes", [2], covering the years 1968–1977, reports any complexes of arsenic with dithiocarboxylates. Therefore we wish to briefly report here the preparation of what appear to be the first complexes of arsenic(III) with some dithiobenzoate ligands:



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where X = Cl, CH_3, or COC_6H_5
a, *b* *c*

The three orange-colored *tris*-chelates (*1a*, *1b*, *1c*) were prepared by treating an ethanol solution of AsI_3 with a 3:1 mol ratio of the tetraalkylammonium salt [3] of the appropriate sulfur ligand. The same procedure, employing the sodium salt of diethyldithiocarbamate, gave light brown crystals of As-$[S_2CN(C_2H_5)_2]_3$ (*2*) in high yields also. Analytical and melting or decomposition data for the new compounds are given in Table I. *1a* exhibited an As–S stretching frequency at 418 cm^{-1} whereas that for *1b* occurred at 435 cm^{-1}, suggesting, but of course not demonstrating, a stronger As–S bond in the latter compound which contains the more strongly electron-donating methyl group in place of the chloro species *para* to the $-CS_2$ group.

TABLE II. NMR Shift Data (ppm) for the As Complexes and the Acid and Ionic Forms of the Ligands.

Compound[a]	*ortho*	*meta*	CH_3
1a	8.19	7.42	–
1a acid	7.96	7.30	–
1b	8.19	7.23	2.38
1b acid	7.93	7.11	2.33
1b salt	8.25	6.97	2.28
1c	8.36	7.88	–
1c acid	8.14	7.79	–
1c salt	8.21	7.75	–

[a] *1a* acid is meant to stand for the acid form of the ligand attached to the As in *1a*; *1b* salt is meant to stand for the tetraalkylammonium salt of the ligand attached to the As in *1b*, *etc.*

Some proton nmr shift data for the new compounds as well as for the corresponding ligands, in both their acid and salt form, is summarized in Table II. The downfield shift of the *ortho* (and *meta*) protons in the complex containing the electron-withdrawing benzoyl group *para* to the CS_2^- is expected due to the deshielding effect of this substituent.

There is recent evidence that arsenic (as well as cadmium, chromium, cobalt and nickel) may be

TABLE I. Analytical and Melting Point (Decomposition) Data.

Compound	Melting Point (Decomposition), °C	Analytical Data[a]			
		C	H	As	S
		Found (Calcd)	Found (Calcd)	Found (Calcd)	Found (Calcd)
1a	134–136	39.49 (39.52)	2.19 (1.90)	12.02 (11.74)	30.30 (30.15)
1b	(74–80)	49.26 (49.98)	4.19 (3.67)	–	–
1c	(78–83)	59.27 (59.55)	3.34 (3.22)	9.05 (8.84)	22.56 (22.71)
2		34.02 (34.67)	5.76 (5.82)	7.85 (8.09)[b]	–

[a] As and S analyses, as well as independent checks on C and H, were performed by Galbraith Labs., Inc., Knoxville, Tenn. [b] Data for elemental nitrogen.

implicated in the epidemiology of human cancers and that these five metals or their compounds may be the most important inorganic carcinogens [4]. Arsenic poisoning also appears to be on the rise and chelate therapy is being studied for it as well as for other type B metal ions [5]. Complexes of arsenic with sulfur-donor ligands are thus prime candidates for increased study.

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