

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

AZIDO-DITHIOCARBONIC ACID.

VI. SALTS OF COPPER, SILVER, GOLD, ZINC, CADMIUM, MERCURY, THALLIUM, LEAD AND BISMUTH^{1,2}

BY G. B. L. SMITH, PAUL WARTTMAN AND A. W. BROWNE

WITH MICROSCOPICAL STUDIES BY C. W. MASON

RECEIVED JUNE 16, 1930

PUBLISHED JULY 3, 1930

One of the outstanding characteristics of azido-dithiocarbonic acid and its derivatives thus far described is the relative ease with which these substances undergo spontaneous thermal decomposition into nitrogen, sulfur and thiocyanic acid or its corresponding derivatives. In some instances the time required for complete decomposition of the substance at ordinary temperatures is but a few hours; in others it is a number of months. Exposure to light appears in certain cases to be an important, if not indeed a controlling factor. In other cases the influence of light seems to be practically negligible.

The sensitivity of the various azido-dithiocarbonates to mechanical impact also varies over a wide range. The ammonium and tetramethylammonium^{2d} salts, for example, do not explode when struck with a hammer; the zinc, bismuth and anhydrous cadmium salts (*vide infra*), on the other hand, detonate, even under water, when subjected to very slight mechanical disturbance. This sensitivity, of the heavy metal azido-dithiocarbonates in particular, may reasonably lead to the expectation that certain of these compounds, suitably stabilized and partially desensitized, should prove to be useful as primers or detonators. In this event the co-existence of the brisant N_3 radical and inflammable atoms in the same molecule should offer an advantage over certain primers of the older type that is reminiscent of the superiority of the modern propellant or high explosive over ordinary black gunpowder. On the theory that the azido-dithiocarbonate radical may in a sense be regarded "as a labile combination of thiocyanogen with [molecular] nitrogen and sulfur,"^{2a} the use of lead azido-dithiocarbonate, for example, as a constituent of a primer would be equivalent to the addition of one molecule of nitrogen and one atom of

¹ For the earlier articles of this series see (a) *THIS JOURNAL*, **45**, 2604 (1923); (b) **47**, 2698 (1925); (c) **49**, 917 (1927); (d) **49**, 2129 (1927); (e) **52**, 1928 (1930). Manuscript received July 26, 1929.

² The investigation upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University. The present paper, which was presented orally and in abstract at the Ithaca meeting of the American Chemical Society in September, 1924, is Article No. 5 under Heckscher Grant No. 60. For articles 1 to 4 see Ref. 1, and also (a) *THIS JOURNAL*, **47**, 1916 (1925). For other literature related to the subject, and published from this Laboratory, see (b) *ibid.*, **44**, 2106 (1922); (c) **44**, 2315 (1922); (d) **44**, 2849 (1922); (e) **45**, 2541 (1923); (f) **48**, 2383 (1926); (g) **49**, 2759 (1927).

sulfur to each molecule of lead thiocyanate, a substance that has already found use in this field.

The heavy metal azido-dithiocarbonates were considered by Sommer³ to be of such enormously explosive character as to render inadvisable any closer investigation. To the authors of the present paper it has nevertheless seemed desirable, and entirely within the range of experimental feasibility, to isolate and describe certain of the typical heavy metal salts, as a preliminary to a more extended study of their explosive character.

In the present article are recorded the results obtained (a) in the preparation and investigation of six new compounds: AgSCSN_3 , $\text{Cd}(\text{SCSN}_3)_2 \cdot 2\text{H}_2\text{O}$, HgSCSN_3 , $\text{Hg}(\text{SCSN}_3)_2$, TlSCSN_3 , and $\text{Pb}(\text{SCSN}_3)_2$; (b) in the qualitative study of the azido-dithiocarbonates of copper, gold, zinc and bismuth, for none of which satisfactory quantitative data were obtained.

Preparation.—The heavy metal salts were prepared by interaction of aqueous solutions containing the azido-dithiocarbonate ion and aqueous solutions containing the respective metallic ion. The freshly prepared free acid^{1a} was used as the source of the azido-dithiocarbonate ions, in place of the sodium salt employed by Sommer,³ since the latter substance has been found more difficult to prepare relatively free from thiocyanate ion. In Table I are presented the analytical data for the compounds isolated.

TABLE I
ANALYTICAL DATA FOR HEAVY METAL AZIDO-DITHIOCARBONATES

Formula	Calcd.	Analyses, %		Constituent weighed as
		Found	Found	
AgSCSN_3	Ag	47.73	47.56, 47.51	AgCl
	SCSN_3	52.27	52.64, 53.06	HSCSN_3
$\text{Cd}(\text{SCSN}_3)_2 \cdot 2\text{H}_2\text{O}$	Cd	29.22	29.58, 29.50	CdS
	S	33.34	33.24, 33.28	BaSO_4
HgSCSN_3	Hg	62.93	63.16, 67.76	HgS
	S	20.12	20.45, 20.23	BaSO_4
$\text{Hg}(\text{SCSN}_3)_2$	Hg	45.96	46.09, 46.01	HgS
	S	29.35	29.41, 29.50	BaSO_4
TlSCSN_3	Tl	63.32	63.13, 63.28	Tl_2PtCl_6
	S	19.90	19.86, 20.02	BaSO_4
$\text{Pb}(\text{SCSN}_3)_2$	Pb	46.72	46.60, 46.61	PbSO_4
	S	28.93	29.03, 28.99	PbSO_4

Properties of the Heavy Metal Azido-dithiocarbonates.—All of the compounds studied are insoluble in water in the ordinary sense of the term. The very low concentration of azido-dithiocarbonate ion present in the filtrate from an aqueous suspension of any of these substances is sufficient,

³ Sommer, *Ber.*, **48**, 1833 (1915); "Die diesbezüglichen Versuche wurden nur qualitativ ausgeführt und auf die Isolierung der reinen Verbindungen Verzicht geleistet, da der enorm explosive Charakter fast aller Schwermetallsalze eine nähere Untersuchung nicht ratsam erscheinen liess."

however, to permit catalysis of the reaction between iodine and potassium trinitride.^{2b}

The azido-dithiocarbonates of copper, silver and univalent mercury are obtained in the form of flocculent precipitates. The azido salts of the other heavy metals, with the exception of gold, are precipitated in distinctive crystalline form. All of the salts, except that of gold which decomposed thermally during the process of drying at room temperature, were found to be sensitive to mechanical shock. Those of copper, silver, mercury (ous and ic), cadmium (hydrated), thallium and lead are obtainable in the dry state without serious hazard, but detonate violently under rather slight mechanical provocation. Those of zinc and bismuth detonate at ordinary temperatures under water during the process of crystallization. From the numerous qualitative observations made it appears that the sensitivity to mechanical impact of compounds of heavy metals in the first and second groups of the periodic system varies inversely, while the brisance of the explosion varies directly with the atomic weight. On the other hand, the sensitivity of compounds of metals in the series mercury to bismuth varies directly and the brisance inversely with the atomic weight.

The behavior of the compounds toward various reagents and solvents is indicated in Table II.

TABLE II
BEHAVIOR OF THE HEAVY METAL AZIDO-DITHIOCARBONATES TOWARD SOLVENTS AND REAGENTS

Legend: D, detonated; V, very soluble, or vigorously attacked; M, moderately soluble, or moderately attacked; S, slightly soluble, or but little attacked; I, insoluble, or unattacked

	C ₂ H ₅ OH	CH ₃ OH	CCl ₄	CS ₂	(C ₂ H ₅) ₂ O	C ₆ H ₆	(CH ₃) ₂ CO	Concd. H ₂ SO ₄	1:6 H ₂ SO ₄	Concd. HNO ₃	1:6 HNO ₃	Concd. HCl	1:6 HCl	Glacial HC ₂ H ₃ O ₂	1:6 HC ₂ H ₃ O ₂	NH ₄ OH soln.	NaOH soln.
AgSCSN ₃	I	I	I	I	I	I	I	V	I	S	I	S	I	I	I	S	S
Cd(SCSN ₃) ₂ ·2H ₂ O	M	M	I	I	M	I	I	D	M	M	M	M	M	S	M	S	S
HgSCSN ₃	I	I	I	I	I	I	I	D	I	M	I	S	I	I	I	M ^a	M ^a
Hg(SCSN ₃) ₂	I ^a	I ^a	I	I	I	I	I ^a	D	I	S	I	S	I	I	I	I ^a	I ^a
TlSCSN ₃	I	S	I	I	I	I	I	D	M	M	M	M	S	I	S	S ^a	S ^a
Pb(SCSN ₃) ₂	I	I	I	I	I	I	I	V	V	V	M	V	V			S	S
Cu salt								V	M	M	M	S				S	S

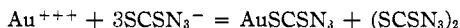
^a Darkened, probably as the result of photochemical action.

Copper Azido-dithiocarbonate.—This salt is yellow (Y) when moist, and dark yellow (YS1) in the solid state. Numerous unsuccessful attempts to obtain a copper compound of uniform⁴ composition indicate that cupric ion interacts with azido-dithiocarbonate ion to form a mixture of cuprous and cupric azido-dithiocarbonates, which undergoes slow thermal decomposition with formation of an inert product, probably consisting of the copper thiocyanates.

⁴ Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, 1905, Vol. I, 1st ed., p. 232.

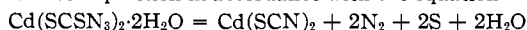
Silver Azido-dithiocarbonate, AgSCSN₃.—This white slightly photosensitive compound, either in aqueous suspension or in the solid state, tends to darken on exposure to light. It is soluble in pyridine, and may be recrystallized from this solvent in rosetts of needle crystals.

Gold Azido-dithiocarbonate.—Auric and azido-dithiocarbonate ions interact in aqueous solution with initial precipitation of azido-carbondisulfide, accompanied by discharge of the yellow color. After one hour a bulky, white, fibrous precipitate fills the entire solution. After sixteen hours this precipitate assumes a dark orange-yellow color (OYS1). Under the microscope it appears as strikingly distorted crystals that grow as bunches of long fibers having the appearance of vegetable fibers. They are anisotropic and show parallel extinction. Characteristic crystals of azido-carbondisulfide may be seen. The solid is in all probability a mixture of aurous azido-dithiocarbonate and azido-carbondisulfide formed in accordance with the equation



Zinc Azido-dithiocarbonate.—After a delay of a few minutes, characteristic of all heavy metal azido salts of this group, a beautifully crystalline precipitate, composed of easily visible regular octahedra, is formed. Various attempts to separate this precipitate from the mother liquor have resulted in explosions, owing to the great sensitivity of the zinc azido salt. Immersion of samples of metallic zinc in an aqueous solution of the free azido acid results in the incrustation of the metal with a yellow solid exceedingly sensitive to friction.

Cadmium Azido-dithiocarbonate Dihydrate, Cd(SCSN₃)₂·2H₂O.—Several subaqueous detonations of this salt have been observed. These may be attributable to initial formation of the very sensitive anhydrous salt which, if it escaped detonation, should subsequently undergo hydration. The dihydrate undergoes slow, spontaneous, quantitative, thermal decomposition in accordance with the equation



Under the microscope the dihydrate appears as long, fine needles with end faces not well formed, apparently oblique, prismatic, with indistinct cross sections. The crystals are strongly doubly refractive, and have a high index of refraction, which prevents sharp observation of the extinction angle. This probably has a maximum value of about 35°. Dispersed extinction appears to be exhibited, and is seen best with thin crystals giving low order polarization colors, which change but do not extinguish at any definite point.

Mercurous Azido-dithiocarbonate, HgSCSN₃.—This substance when first formed is of a dark brown color, but when stirred the suspended precipitate becomes white. Preliminary preparations were found by analysis to consist of a mixture of the mercurous salt and free mercury.

Mercuric Azido-dithiocarbonate, Hg(SCSN₃)₂.—An aqueous suspension of this substance shows something of the appearance of "watered silk." The salt undergoes spontaneous thermal decomposition at room temperature, yielding as a final product mercuric thiocyanate which when ignited gives the characteristic "Pharaoh's serpents."

Thallos Azido-dithiocarbonate, TlSCSN₃.—This is a very light yellow (YT2) crystalline solid which under the microscope appears as dendritic and skeletal forms of oblique formation. The prevailing angle between branches is about 45°. The forms exhibit oblique extinction, and show gray polarization colors, with some light yellow. The refractive index is fairly high. No clean-cut single forms are evident.

Lead Azido-dithiocarbonate, Pb(SCSN₃)₂.—This compound which was obtained in the form of a very light greenish-yellow (GYT2) crystalline solid was deemed sufficiently stable for use in the gravimetric determination of the azido-dithiocarbonate ion. Weighed samples of the sodium azido salt dihydrate were dissolved in 100 cc. of water,

and treated with an excess of lead acetate in aqueous solution. The precipitate was filtered on a tared Gooch crucible, washed with water, alcohol and ether, dried over phosphoric anhydride and weighed.

Anal. Subs., 0.3920, 0.2417: $\text{Pb}(\text{SCSN}_3)_2$ obtained, 0.4916, 0.3026. $\text{NaSCSN}_3 \cdot 2\text{H}_2\text{O}$ found: 0.3927, 0.2418.

When precipitated directly on the microscope slide the lead azido salt at first appears as rosetts of fine, highly birefringent needles, the tiniest of which show brilliant polarization colors. When formed more slowly, or when allowed to stand, the crystals assume the form of lath-shaped prisms, often turned in X's and rosetts. Thickened crystals show yellow by transmitted light. Unit prism and basal pinacoid forms are seen. The forms with oblique ends show oblique extinction, the apparent extinction angle being about 19° . In oblique-ended forms the end angle in the plane of the prism face is about 68° . Forms showing pointed ends show parallel extinction. The crystals are in all probability monoclinic.

Bismuth Azido-dithiocarbonate.—This azido salt is obtained as a light yellow (YT1–YT2) precipitate when bismuth nitrate acidified with nitric acid interacts with the azido-acid in aqueous solution. During subsequent treatment with water the color deepens to a reddish-orange (RO). Under certain conditions the precipitate shows the deeper color at the outset. These precipitates are highly sensitive and have been observed to detonate under water.

Summary

Six heavy metal salts of azido-dithiocarbonic acid have been prepared and described: silver azido-dithiocarbonate, AgSCSN_3 ; cadmium azido-dithiocarbonate dihydrate, $\text{Cd}(\text{SCSN}_3)_2 \cdot 2\text{H}_2\text{O}$; mercurous azido-dithiocarbonate, HgSCSN_3 ; mercuric azido-dithiocarbonate, $\text{Hg}(\text{SCSN}_3)_2$; thalious azido-dithiocarbonate, TlSCSN_3 ; and lead azido-dithiocarbonate, $\text{Pb}(\text{SCSN}_3)_2$. Qualitative observations have been made upon the corresponding salts of copper, gold, zinc and bismuth.

Azido-dithiocarbonates of the heavy metals in the first and second groups of the periodic system show a sensitivity to mechanical impact that varies inversely, while the brisance of the explosion varies directly with the atomic weight. On the other hand, the sensitivity of compounds of metals in the series mercury to bismuth varies directly and the brisance inversely with the atomic weight.

ITHACA, NEW YORK