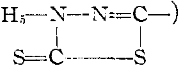
Metal Salts of 2-Mercapto-4-phenyl-Δ^2-1,3,4-thiadiazoline-5-thione

BY GEORGE W. WATT AND MARY E. BOYD

Metal salts of 2-mercapto-4-phenyl-Δ^2-thiadiazoline-5-thione (represented as RSH, where R is  $\begin{array}{l} C_6H_5\text{—}N\text{—}N\text{=}C\text{—} \\ \qquad\ \ | \qquad\quad | \\ \quad\ S\text{=}C\text{———}S \end{array}$) have been prepared by Ray[1a] and by Ray and Guha.[1b] More recently the possible use of these salts in qualitative and quantitative analysis has been suggested.[2] The present note is concerned with the preparation of unreported salts of RSH and with the formation of coördination compounds of these salts upon treatment with ammonia, pyridine and ethylenediamine (en).

Experimental

The salt RSK was prepared according to the method of Busch.[3] Repeated crystallization from absolute ethanol gave an 85% yield of the white crystalline salt, m. p. 245°; reported by Busch, 240°.

Anal. Calcd. for $C_8H_5N_2S_3K$: N, 10.6. Found: N, 10.4.

The heavy metal salts of RSH were formed at room temperature by addition of an aqueous solution of slightly more than one equivalent of the specified inorganic salt to an agitated aqueous solution of 1/40 mole of RSK. The precipitated salts were separated by filtration, purified by repeated extraction with water, ethanol and acetone, and dried *in vacuo* over concentrated sulfuric acid. When the dry salts were heated, slow decomposition occurred and none exhibited a sharp melting temperature. However, with nickel chloride the normal salt was precipitated only after four hours of heating and the use of nickel nitrate or sulfate resulted largely in the formation of the disulfide, RSSR, m. p. 124°.

The reaction between RSK and mercury (II) cyanide in absolute ethanol led to the formation of a double salt of the type $(RSK)_2Hg(CN)_2$ which was converted to the yellow normal mercury (II) salt upon treatment with water. When the same reactants were brought together in aqueous solution they reacted to form a white solid (presumably the double salt) which decomposed yielding the normal yellow salt slowly at room temperature and more rapidly at elevated temperatures. When mercury (II) bromide was used, the normal yellow salt was obtained immediately.

The salts were insoluble in water and in the common organic solvents, soluble or sparingly soluble in liquid ammonia, and soluble (usually with decomposition) in pyridine or ethylenediamine. Coördination compounds with ammonia were formed by allowing the excess solvent to evaporate from solutions of the salts in liquid ammonia. Coördination compounds with ethylenediamine were precipitated by diluting solutions of the heavy metal salts in that solvent with water. In the di-solvate $(RS)_2Hg(en)_2$ the central mercury atom is presumably 6-covalent. Coordination compounds of reproducible composition were obtained only after extended desiccation *in vacuo* over concentrated sulfuric acid at room temperature. Stable solvates with pyridine were not obtained in any case.

TABLE I

METAL SALTS OF 2-MERCAPTO-4-PHENYL-Δ^2-1,3,4-THIADIAZOLINE-5-THIONE AND THEIR COÖRDINATION COMPOUNDS ($R = C_8H_5N_2S_2$)

Product	Inorg. salt	Yield	Color	Percentage composition Nitrogen Calcd.	Percentage composition Nitrogen Found	Percentage composition Metal Calcd.	Percentage composition Metal Found	Coörd. cpd. with	Color	Nitrogen, % Calcd.	Nitrogen, % Found
$(RS)_2Hg$[a,b]	$HgBr_2$	Quant.	Yellow	8.6	8.8	30.8	31.0	0.5 NH_3	Yellow	9.6	9.7
$(RS)_2Hg$[c]	$Hg(CN)_2$	....	Yellow	8.6	8.6	30.8	30.4	......	.....	..	..
$(RS)_2Cu$[d]	$CuSO_4$	Quant.	Orange[e]	10.7	10.7	12.4	12.7	NH_3	Dk. br.	12.9	13.0
$(RS)_2Ni$	$NiCl_2$	[f]	Brown	11.0	11.0	11.5	11.4	NH_3[g]	Dk. br.	13.3	13.1
RS Ag[h]	$AgNO_3$	Quant.	Yellow	8.4	8.6	32.4	32.5	0.5 en[i]	Cream	..	..

[a] M. p., 110° (dec.). [b] Coörd. cpd. with 2 en: formed after forty-eight hours of desiccation over concd. sulfuric acid; color, white. *Anal.* Nitrogen %, calcd. 14.6; found 14.5. Coörd. cpd. with 1 en; formed after one hundred and forty hours desiccation: color, white; *anal.* nitrogen %, calcd. 11.8; found, 11.8. [c] After decompn. of the white double salt which formed first. [d] Small amounts of disulfide, RSSR, formed as by-product. [e] After heating at 90° for one hour; original ppt. was tan. [f] Precipitated only after four hours of heating. Original dark brown ppt. lightened in color as heating continued. [g] An olive-green ppt. (probably a higher ammonate) formed first but was not isolated. [h] Dec. on exposure to light, air or hot ethanol; m. p. 150° (dec.). [i] Some evidence for the formation of a compound corresponding to this formula was obtained but analytical data on separate preparations were not conclusive.

Data relative to the metal salts and their coördination compounds are given in Table I.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF TEXAS
AUSTIN, TEXAS

RECEIVED FEBRUARY 18, 1946

---

(1) (a) Ray, *J. Chem. Soc.*, **115**, 875 (1919); (b) Ray and Guha, *ibid.*, **115**, 261 (1919).

(2) (a) Majumdar, *J. Indian Chem. Soc.*, **19**, 396 (1942); (b) Kuras, *Chem. Obzor.*, **16**, 17, 124 (1941).

(3) Busch, *Ber.*, **27**, 2510 (1894).