[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF SYDNEY]

Bidentate Chelate Compounds. I

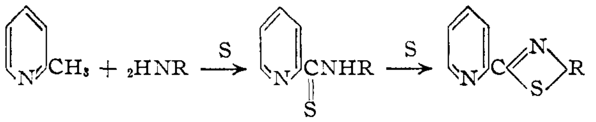
BY FRANCIS LIONS AND KENNETH V. MARTIN[1]

RECEIVED OCTOBER 2, 1957

Some new α-thiopicolinamides have been synthesized and shown to function as bidentate chelate compounds.

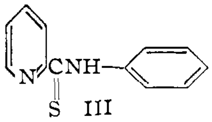
Diehl,[2] in his review of chelate compounds, has pointed out that the bidentate chelate compounds constitute the largest group and are the most thoroughly studied. A recent report[3] of a convenient method for the preparation of α-thiopicolinanilide suggested that this substance and some of its analogs should be able to function as bidentate chelate compounds. Because, further, there do not appear to be any reports of studies of similarly constituted bidentates it was thought of value at least to make some preliminary studies of such compounds.

α-Thiopicolinanilide (I, R = phenyl) was prepared according to the method described by Porter[3] and was obtained as an orange crystalline solid. This procedure involves heating excess α-picoline with sulfur and aniline for many hours. The reaction proceeded readily also when such bases as *o*-toluidine, *m*-toluidine, *p*-anisidine, α-naphthylamine and 2-aminopyridine were substituted for aniline (see Table I). However, the reaction apparently failed with *o*-anisidine and β-naphthylamine. It is interesting to note that if excess sulfur was used, then on attempted isolation of the product by vacuum distillation, the corresponding benzothiazole II was obtained. Similarly, the benzothiazoles could be prepared readily by distilling a mixture of the pure α-thiopicolinamide and sulfur *in vacuo*.

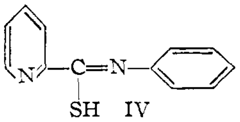


I II

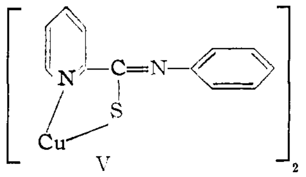
When a methanol solution of copper(II) acetate was added to an alcoholic solution of α-thiopicolinanilide a dull red color developed and bis-(α-thiopicolinanilide)-copper(II) crystallized from solution in lustrous bronze-red plates, m.p. 205°. The copper(II) complex behaved as a typical uncharged complex and could be recrystallized from a chloroform–ethanol mixture. Since the copper(II) complex is non-charged and contains two moles of I (R = C_6H_5–) it can be formulated as V. α-Thiopicolinanilide, in its reaction, functions as either of the tautomeric forms III or IV. The thiol form IV reacts with copper(II) ions to form V. Similar complexes (involving two moles of IV coördinated to one atom of the metal) can be prepared containing coördinated nickel(II), zinc(II) and mercury(II). Silver(I) and lead(II) salts apparently cause decomposition of the organic molecule and formation of the metal sulfide as a precipitate.



III



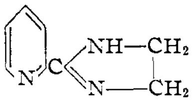
IV



V

Alterations in the type of amine used to prepare the α-thiopicolinamide do not apparently affect the coördinating power: α-thiopicolin-*o*-toluidide, α-thiopicolin-*m*-toluidide, α-thiopicolin-*p*-toluidide, α-thiopicolin-*p*-anisylamide and α-thiopicolin-α-naphthylamide formed similar metal complexes (see Table II).

When α-thiopicolinanilide and ethylenediamine were heated together under reflux the solution acquired a deep red color and hydrogen sulfide was evolved. Vacuum distillation produced 2-(α-pyridyl)-imidazoline (VI) in 71% yield. This reaction of ethylenediamine with thioamides was first utilized by Forsell[4,5] and provides a convenient method for synthesis of imidazolines. VI is of interest in that it functions as a bidentate chelate compound in a similar manner to dipyridine and *o*-phenanthroline.[6] The preparation described above represents a very convenient method for the synthesis of VI. This could be of value since methods for the colorimetric determination of iron have been evolved using VI as reagent.[6]



VI

Experimental[7]

α-Thiopicolinamides (see Table I) were prepared according to the method described by Porter.[3] The amine (2 moles), α-picoline (1 mole) and sulfur (1.5 moles) were heated for from 6 to 48 hours in an oil-bath maintained at 160–180°. The product usually was isolated by vacuum distillation. When the amine used was *m*-toluidine, *p*-toluidine or *p*-anisidine this treatment resulted in formation of the corresponding benzthiazole. However the α-thiopicolinamide could be isolated by careful crystallization of the crude reaction product from ethanol.

Preparation of Bis-α-thiopicolinamido-Metal Complexes.—To a solution of the α-thiopicolinamide (2 mole) in ethanol was added a methanol solution of the metal acetate (1 mole). Generally the metal complex separated immediately. This was collected and recrystallized from a chloroform–ethanol mixture.

---

[1] University Research Fund Student of the University of Sydney. Inquiries regarding this paper should be sent to K. V. Martin, Polychemicals Department, E. I. du Pont de Nemours and Co., Wilmington, Del.

[2] H. Diehl, *Chem. Revs.*, **21**, 39 (1937).

[3] H. D. Porter, THIS JOURNAL, **76**, 127 (1954).

[4] Forsell, *Ber.*, **24**, 1846 (1891).

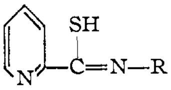
[5] Forsell, *ibid.*, **25**, 2135 (1892).

[6] J. L. Walter and H. Frieser, *Anal. Chem.*, **26**, 217 (1954).

[7] All melting points are uncorrected.

TABLE I

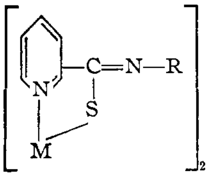
α-THIOPICOLINAMIDES



No.	R	M.p., °C.	Yield, %	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
1	Phenyl	46.5	71	$C_{12}H_{10}N_2S$						
2	*o*-Toluyl	69.5	75	$C_{13}H_{12}N_2S$	68.4	68.6	5.3	5.5		
3	*m*-Toluyl	80	44	$C_{13}H_{12}N_2S$	68.4	68.4	5.3	5.2	12.3	11.8
4	*p*-Toluyl	98.5	55	$C_{13}H_{12}N_2S$	68.4	68.4	5.3	5.2		
5	*p*-Anisyl	100.5	86	$C_{13}H_{12}NO_2S$	63.8	63.9	5.0	5.0	11.4	11.2
6	α-Naphthyl	133	22	$C_{16}H_{12}N_2S$	61.4	61.8	4.2	4.3		
7	α-Pyridyl	81.5	22	$C_{11}H_{12}N_2S$					19.5	18.7

TABLE II

METAL COMPLEXES DERIVED FROM α-THIOPICOLINAMIDES



No. (see Table I)	Metal (M)	Form	M.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Metal, % Calcd.	Metal, % Found
1	Copper (II)	Bronze plates	205	58.8	58.9	3.7	3.7	13.0	12.8
	Nickel (II)	Yellow needles	242	59.4	59.2	3.7	3.6		
	Mercury (II)	Yellow needles	174	46.0	46.2	2.9	2.9		
	Zinc (II)	Yellow tablets	265	58.6	58.5	3.7	3.7		
2	Copper (II)	Brown flakes	220	60.2	60.2	4.3	4.3	12.4	12.5
	Nickel (II)	Bronze flakes	271	60.8	60.5	4.3	4.5		
	Mercury (II)	Yellow prisms	173	47.6	47.6	3.4	3.5		
3	Copper (II)	Brown plates	174	60.2	59.9	4.3	4.3		
	Nickel (II)	Bronze plates	229	60.8	60.5	4.3	4.4		
	Mercury (II)	Yellow prisms	122	47.6	47.6	3.4	3.5		
4	Copper (II)	Brown plates	209	60.2	60.2	4.3	4.3	12.4	12.6
	Nickel (II)	Bronze plates	258	60.8	60.8	4.3	4.3		
	Mercury (II)	Yellow prisms	163	47.6	47.5	3.4	3.4		
5	Copper (II)	Brown plates	209	56.7	56.1	4.0	4.3	11.5	11.3
	Nickel (II)	Bronze plates	245	57.2	57.2	4.0	4.0		
	Mercury (II)	Yellow powder	156	45.5	45.5	3.2	3.4		
6	Copper (II)	Brown microcrystals	194	65.1	63.7	3.7	3.7		
	Nickel (II)	Bronze plates	260	65.6	63.4	3.8	3.7		
	Mercury (II)	Yellow prisms	204	52.8	51.7	3.0	3.3		

2-(α-Pyridyl)-imidazoline.—α-Thiopicolinanilide (72.0 g., 0.35 mole) and ethylenediamine (30 g., 0.5 mole) were heated together under reflux for 30 minutes. The reaction mixture colored deep red and hydrogen sulfide was evolved. Distillation *in vacuo* yielded 2-(α-pyridyl)-imidazoline (75 g., 71% of theory) as a colorless oil (b.p. 140° (1 mm.)) which soon solidified. It crystallized from a benzene–petroleum ether mixture in colorless plates, m.p. 100–101°.

Anal. Calcd. for $C_8H_9N_3$: C, 65.3; H, 6.2. Found: C, 65.1; H, 6.1.

The picrate crystallized in long yellow needles from a water–alcohol mixture, m.p. 228°.

Anal. Calcd. for $C_{14}H_{12}N_6O_7$: C, 44.7; H, 3.2. Found: C, 44.5; H, 3.4.

Acknowledgment.—The authors gratefully acknowledge the assistance of Miss B. Stevenson, who carried out all the C, H and N microanalyses, and Mr. J. Croft, who gave preparative assistance.

SYDNEY, AUSTRALIA