

half of the material which it dissolved at boiling temperature. In methyl alcohol or ethyl acetate solution the methyl ester tended to oxidize readily and to turn green. The crude ester melted at about 180–190° and did not appear to decompose at this temperature. At distinctly higher temperatures it decomposed to yield a red residue and to produce a very offensive odor. Recrystallization from acetone or methyl alcohol raised the melting point of the material, 197–202°, 202–207°, 203–209°, etc., and in one instance 216–217°. The latter material showed almost no red color when heated to its melting point.

Chlorine was determined by dissolving a sample of the ester in ammonia water and precipitating as silver chloride in the presence of dilute nitric acid. Copper was determined electrolytically in the solution which resulted from treating the ester with concd. nitric acid and diluting with water. The residual liquid gave no test for phosphate with ammonium molybdate, for the trivalent phosphorus had not been oxidized by the cold concd. nitric acid. Experiment showed that evaporation to dryness with concd. nitric acid, or evaporation to fuming with concd. sulfuric acid, would not accomplish the result. Satisfactory phosphorus determinations were finally made by evaporating the sample with a mixture of nitric and sulfuric acids until fumes of sulfuric acid were given off, or by evaporating with fuming sulfuric acid until the liquid

boiled freely, and then diluting with water, precipitating as magnesium ammonium phosphate, etc.

Anal. Calcd. for $\text{CuCl}\cdot\text{P}(\text{OCH}_3)_3$: Cl, 15.89; Cu, 28.49; P, 13.91. Found: Cl, 15.36, 16.26, 16.00; Cu, 28.69, 28.63; P, 13.60, 13.59, 14.22, 13.87, 13.41.

Summary

Phosphorus trichloride combines directly with cuprous chloride to form the compound $(\text{CuCl})_2\cdot\text{PCl}_3$.

The dissociation pressure of this compound has been measured from 0 to 50°. The affinity which holds the phosphorus trichloride in combination with the cuprous chloride is practically constant over that temperature range.

The complex reacts with methyl alcohol, losing one of its molecules of cuprous chloride and forming a complex ester $\text{CuCl}\cdot\text{P}(\text{OCH}_3)_3$.

The pyrolysis of the complex ester yields metallic copper, methyl chloride and volatile compounds of phosphorus which we have not yet identified.

CAMBRIDGE, MASS.

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Metal Pyridine Complex Salts. V.¹ Volume Change During Formation of Cyanates and Thiocyanates

BY TENNEY L. DAVIS AND ALBERT V. LOGAN

The fact that cobaltous thiocyanate forms compounds only with two and with four molecules of pyridine, while cobaltous cyanate forms compounds with two, with four, and with six molecules, has suggested that the affinity of pyridine for the metal in complex thiocyanates is probably less than it is in the complex cyanates. Experiments reported in the second and third papers of this series showed that cobaltous, cupric and nickelous pyridine cyanates have lower dissociation pressures than the corresponding thiocyanates containing the same number of pyridine molecules—and support the conclusion that the pyridine coordinately attached to the metal is held in the complex cyanates by a stronger affinity than it is held in the complex thiocyanates. The substitution of an oxygen atom in place of a sulfur at the remote end of the electrovalently connected acid radical considerably increases the residual affinity of the metal atom available for

combination with pyridine through its coordination valence.

We now find that the greater forces of affinity at work in the complex cyanates, by pulling the parts of the molecules more closely together, produce greater contractions than do the forces which hold together the complex thiocyanates. The proportionate decrease in volume when the complex cyanate is formed from the simple salt plus pyridine is greater than when the complex thiocyanate is similarly formed. The cyanate radical, then, exhausts to a less extent than the thiocyanate radical the total affinity of the metal atom, and leaves more of it available for holding the pyridine with those internal forces which reduce both the dissociation pressure and the volume of the resulting compounds.²

The fact that water and all organic liquids (ex-

(1) Earlier papers of this series: I, Davis and Logan, *THIS JOURNAL*, **50**, 2493 (1928); II, Davis and Batchelder, *ibid.*, **52**, 4069 (1930); III and IV, Davis and Ou, *ibid.*, **56**, 1061, 1064 (1934).

(2) Compare the ideas of T. W. Richards on compressible atoms developed in his Faraday Lecture, delivered before the Chemical Society of London June 14, 1911, and in his Presidential Address to the American Chemical Society, published in *THIS JOURNAL*, **36**, 2417–2439 (1914), where a bibliography of his papers on the subject is also printed.

cept pyridine) which we have tried removed some of the pyridine from the complex salts, and also dissolved more or less of them, greatly limited the choice of liquids which might be used in the density determinations, and practically confined the choice to saturated solutions of the complexes in pyridine itself. This meant that it was generally possible to work only with the most highly pyridinated of the compounds. We have therefore determined the densities at 25° of cupric, nickelous and cobaltous hexapyridine cyanates and tetrapyrindine thiocyanates, by measuring in a pycnometer the amount of a saturated solution of the complex in pyridine (the density of that solution having been determined previously) which was displaced by a known weight of each of the complex salts. The densities of the simple cyanates and thiocyanates were determined similarly under benzene. From the densities, the molecular volumes at 25° of the complexes, of the simple salts, and of the pyridine with which the latter combine to form the complexes have been calculated, and the shrinkages which occur during the formation of the complexes have been determined, and are reported in Table I.

TABLE I
VOLUME CHANGE DURING FORMATION OF COMPLEX
CYANATES AND THIOCYANATES

	Molecular volumes at 25°, cc.			Complex	Volume decrease	Decrease, %
	Pyridine	Salt	Total			
Cu(NCO) ₂ ·6Pyr.	485.0	61.0	546.0	486.3	59.7	10.9
Co(NCO) ₂ ·6Pyr.	485.0	58.8	543.8	474.7	69.1	12.7
Ni(NCO) ₂ ·6Pyr.	485.0	62.0	547.0	469.2	77.8	14.2
Cu(NCS) ₂ ·4Pyr.	323.3	76.2	399.5	366.7	32.8	8.2
Co(NCS) ₂ ·4Pyr.	323.3	73.9	397.2	354.5	42.7	10.7
Ni(NCS) ₂ ·4Pyr.	323.3	73.2	396.5	352.7	43.8	11.1

From these data it appears that the absolute shrinkage in cc. and the per cent. shrinkage calculated on the basis of the volume of the components are both greater for the hexapyridine cyanates than for the tetrapyrindine thiocyanates. The per cent. shrinkage during the formation of cupric hexapyridine cyanate (10.9) is 1.33 times the per cent. shrinkage during the formation of cupric tetrapyrindine thiocyanate (8.2); the ratio for the cobaltous compounds is 1.19, for the nickelous compounds 1.28; average 1.27; that is, the per cent. shrinkage during the formation of cupric, cobaltous and nickelous hexapyridine cyanates from the simple salts and pyridine is about 1.27 times the per cent. shrinkage during the formation of the corresponding tetrapyrindine thiocyanates. The shrinkage, however, in the

case of the hexapyridine cyanates involves six molecules of pyridine while that in the case of the tetrapyrindine thiocyanates involves only four. If each molecule of pyridine in all of the compounds were compressed by the respective chemical forces in exactly the same amount, the absolute shrinkage in cc. during the formation of the hexapyridine cyanates would be 1.5 times the absolute shrinkage during the formation of the tetrapyrindine thiocyanates. The ratios calculated from the data are for the cupric compounds 1.82, for the cobaltous 1.62, and for the nickelous 1.78; average 1.74, or about 16% more shrinkage for each molecule of pyridine combined in the complex cyanates than for each molecule combined in the complex thiocyanates. The absolute shrinkages per mole of combined pyridine are shown in Table II where they are compared with the dissociation pressures of the several substances.

TABLE II
SHRINKAGE DURING COMBINATION WITH PYRIDINE COM-
PARED WITH DISSOCIATION PRESSURE OF THE COMPLEX

	Shrinkage, cc., per mole of combined pyridine	Dissociation pressure, mm.			
		20°	25°	30°	50°
Cu(NCO) ₂ ·6Pyr.	9.9	7.0	10.0	13.4	49.6
Co(NCO) ₂ ·6Pyr.	11.5	5.8	(7.7)	10.0	25.7
Ni(NCO) ₂ ·6Pyr.	13.0	...	5.0	..	7.3
Cu(NCS) ₂ ·4Pyr.	8.2	5.1	(8.4)	12.0	58.0
Co(NCS) ₂ ·4Pyr.	10.7	1.9	(2.6)	3.4	10.6
Ni(NCS) ₂ ·4Pyr.	11.0	5.0	(5.4)	6.1	9.8

The shrinkage per mole of pyridine during the formation of the complexes of the three metals is least for the cupric salt, next for the cobaltous, and most for the nickelous salt—both in the hexapyridine cyanate and in the tetrapyrindine thiocyanate series. For the cyanates the dissociation pressures at 25° (the figures in parenthesis being estimated) fall in the inverse order; the complex showing the greater shrinkage has the lower dissociation pressure. The dissociations of the thiocyanates at 25° do not fall in line; at 50°, however, they are in the inverse order of the shrinkages.

Correction.—The facts that cupric, cobaltous, and nickel cyanates behave alike in forming complexes with six molecules of pyridine, and that cobaltous and nickelous thiocyanates behave alike in forming complexes with four, have led us to believe, contrary to previously existing information, that cupric thiocyanate also forms a complex with four molecules of pyridine. In the

second paper of this series Davis and Batchelder¹ reported analyses and dissociation pressures for the complexes of cupric thiocyanate with one and with two molecules of pyridine. We now find that the dissociation pressures which they reported for the dipyridine compound are actually those of the tetrapyridine compound. They isolated and analyzed the dipyridine compound but failed to observe its dissociation pressure. Their data for the monopyridine compound are correct. The correct data for the three complexes are now summarized in Table III.

TABLE III
DISSOCIATION PRESSURES OF CUPRIC PYRIDINE THIOCYANATES

Temp., °C.	Dissociation pressures, mm.					
	20	30	40	50	60	70
Cu(NCS) ₂ ·4Pyr.	5.1	12.0	27.0	58.0	106.0	..
Cu(NCS) ₂ ·2Pyr.	...	5.0	10.0	23.0
Cu(NCS) ₂ ·Pyr.	...	3.4	5.0	10.1	20.0	36.0

Experiments

The pyridine was fractionated twice, and the portion boiling between 115.25 and 115.40° taken for the density determination.

The complex salts were prepared as described in earlier papers, crystallized from chloroform containing pyridine, dried superficially between filter papers, and kept in desiccators containing pyridine and potassium hydroxide.

Cupric tetrapyridine thiocyanate exists in very dark moss-green crystals which lose pyridine rapidly in the air to produce the dipyridine compound. *Anal.* Calcd. for Cu(NCS)₂·4Pyr: Cu, 12.82; pyridine, 63.77. Found: Cu, 13.05, 12.99; pyridine, 63.98, 64.96. Cupric dipyridine thiocyanate has an emerald-green color and loses pyridine slowly to form the monopyridine compound. *Anal.* Calcd. for Cu(NCS)₂·2Pyr: Cu, 18.80. Found: Cu, 18.74, 18.90. The change to the monopyridine compound is hastened by subjecting the dipyridine compound to reduced pressure. *Anal.* Calcd. for Cu(NCS)₂·Pyr: Cu, 24.58. Found: Cu, 24.34, 23.56. The compounds are only moderately soluble in chloroform, but dissolve more readily if pyridine is added. The substances which were described by Davis and Batchelder were the mono- and dipyridine compounds,

Cupric, cobaltous and nickelous cyanates were prepared by warming the complex salts and pumping off the pyridine. It was found that temperatures above 80° caused decomposition with the production of carbon dioxide and the cyanides of the metals. At lower temperatures it was necessary to continue the pumping for several days in order to remove all of the pyridine. Cupric cyanate has a dark moss-green color, nickelous cyanate pale green, and cobaltous cyanate pale lavender.

Cobaltous thiocyanate was prepared as a yellow-brown powder by heating the pyridine complex in vacuum at about 300° at which temperature no decomposition of the salt was found to occur. Nickelous thiocyanate, mustard yellow, was procured by heating the pyridine complex in a well ventilated oven at 250° for two or three hours.

Cupric thiocyanate could not be prepared by any of these methods. It breaks down at slightly elevated temperatures to produce a reddish-brown compound which has been described by Speter³ as having the composition Cu(CNS)₂·CuCNS. When precipitated from aqueous solution, it decomposes to a greater or less extent forming cuprous thiocyanate. We have prepared the substance by treating freshly precipitated and moderately dry cupric hydroxide with the very strong thiocyanic acid procured by distilling potassium thiocyanate, phosphorus pentoxide and concd. sulfuric acid in an atmosphere of hydrogen at about 60 mm. pressure.⁴ The intensely black cupric thiocyanate was transferred quickly to a suction filter, the excess acid was removed, and the unwashed solid was dried in a desiccator over concd. sulfuric acid.

The composition of the salts was verified by analysis for the metals. Cobalt was determined as sulfate, copper by titration with iodide and sodium thiosulfate, and nickel by titration with potassium cyanide. Results are summarized in Table IV.

TABLE IV
ANALYSIS OF CYANATES AND THIOCYANATES

	Metal, %		Calcd.
	Found	Calcd.	
Cupric cyanate	42.84	43.47	43.08
Nickelous cyanate	41.24	41.09	41.13
Cobaltous cyanate	41.16	41.98	41.23
Cupric thiocyanate	35.59	35.50	35.40
Nickelous thiocyanate	33.50	33.57	33.59
Cobaltous thiocyanate	33.61	33.55	33.69

The densities at 25° of the simple salts, and of the complexes except nickelous tetrapyridine thiocyanate, were determined as has been described briefly in the early part of the present paper. Nickelous tetrapyridine thiocyanate when allowed to stand in contact with pure pyridine forms the heptapyridine derivative which has been described in the second paper of this series.¹ It is unaltered even by long standing in contact with its solution in a 60/40 mixture of pyridine and benzene, and its density was determined by the use of this solution. The density determinations are summarized in Table V.

TABLE V
DENSITIES AT 25°

	Experimental values		Average
	0.9774	0.9772	
Pyridine	0.9774	0.9772	0.9773
Cu(NCO) ₂	2.4195	2.4172	2.418
Ni(NCO) ₂	2.3018	2.3021	2.302
Co(NCO) ₂	2.4325	2.4322	2.432
Cu(NCS) ₂	2.3589	2.3536	2.356
Ni(NCS) ₂	2.3866	2.3845	2.386
Co(NCS) ₂	2.3673	2.3656	2.366
Cu(NCO) ₂ ·6Pyr.	1.2781	1.2780	1.278
Ni(NCO) ₂ ·6Pyr.	1.3142	1.3147	1.314
Co(NCO) ₂ ·6Pyr.	1.2995	1.2994	1.299
Cu(NCS) ₂ ·4Pyr.	1.3511	1.3509	1.351
Ni(NCS) ₂ ·4Pyr.	1.3922	1.3901	1.391
Co(NCS) ₂ ·4Pyr.	1.3846	1.3844	1.384

(3) Speter, *Z. Med. Chem.*, **3**, 14; *Chem. Zentr.*, **96**, 1, 2089 (1925).
(4) Rosenheim and Levy, *Ber.*, **40**, 2166 (1907).

Summary

The decreases in volume which occur at 25° when cupric, cobaltous and nickelous cyanates and thiocyanates combine with pyridine to form hexapyridine cyanates and tetrapyridine thiocyanates have been determined.

The shrinkage in cc. during the formation of the hexapyridine cyanates is about 1.74 times as great as during the formation of the tetrapyridine thiocyanates. This corresponds to about 16% more shrinkage for each molecule of pyridine in the complex cyanates than for each molecule in the complex thiocyanates. This fact, and the fact that the complex cyanates have the lower

dissociation pressures, both indicate that the pyridine in the complex cyanates is held by greater forces of chemical affinity than in the complex thiocyanates. The thiocyanate radical to a greater extent than the cyanate radical exhausts the total affinity of the metal atom and leaves less of it available for coordinative combination with pyridine.

For the three cyanates and thiocyanates alike, the shrinkage during combination with pyridine is least in the case of the cupric compounds, next in the case of the cobaltous, and most in the case of the nickelous compounds.

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The Heats of Dissociation of Hexaarylethanes

BY CHARLES BUSHNELL WOOSTER

In a recent paper Conant¹ has estimated the heats of dissociation of a number of substituted ethanes from cryoscopic data on the basis of the following assumptions: (1) that the heat of dissociation, ΔH , the free energy of dissociation, ΔF , and the corresponding entropy change, ΔS , were all approximately independent of the nature of the solvent in which the ethane was dissolved; (2) that ΔH and ΔS were independent of the temperature over the range involved in the experiments and (3) that ΔS was independent of the substituents attached to the two carbon atoms which dissociate from each other, at least in solution in organic solvents. The work of Ziegler,² on hexaphenylethane had furnished confirmation of the first two assumptions, but Conant offered no experimental basis for the third. The last assumption has also been made by Pauling and Wheland³ but, on the other hand, Hückel⁴ states that variations in the entropy change may be expected to accompany alterations in the structure of the molecules.

As a matter of fact, it is possible to calculate values for the heats of dissociation of four hexaarylethanes by independent and somewhat more direct methods from data at present available in

the literature. It is the purpose of this paper to present and discuss the results of such calculations.

The Heat of Dissociation of Di- β -naphthyltetraphenylethane.—Gomberg and Sullivan⁵ have measured the intensity of color of solutions of di- β -naphthyltetraphenylethane over a wide temperature range in toluene and in chloroform solutions. A sufficiently close approximation to the dissociation constant K , expressed in mole fractions, may be obtained from these measurements by the use of equation 1

$$K = \frac{4N(I/I_0)^2}{1 - I/I_0} \quad (1)$$

where N is the concentration in moles of the ethane per mole of solvent, I is the intensity of color per mole of the ethane (in arbitrary units) and I_0 is the limiting value of I on dilution.⁶ In order to test the consistency of the data, ΔH is best determined graphically by plotting values of $-\log K$ against $1/T$ which should yield a straight line in accordance with equation 2

$$-\log K = (\Delta H/2.303RT) + \text{const.} \quad (2)$$

when ΔH is independent of the temperature. The value $I_0 = 195$ was obtained from equation 1 by setting K equal to the value 3.50×10^{-4} based on Ziegler's photometric measurements at 20° in

(1) Conant, *J. Chem. Phys.*, **1**, 427 (1933).

(2) Ziegler, *Ann.*, **373**, 163 (1929).

(3) Pauling and Wheland, *J. Chem. Phys.*, **1**, 362 (1933).

(4) Hückel, "Free Radicals, a General Discussion." The Faraday Society, 1933, p. 40.

(5) Gomberg and Sullivan, *THIS JOURNAL*, **44**, 1810 (1922).

(6) The value of I_0 is assumed to be independent of the temperature and of the nature of the solvent. These assumptions were also made by Ziegler in his study of hexaphenylethane.