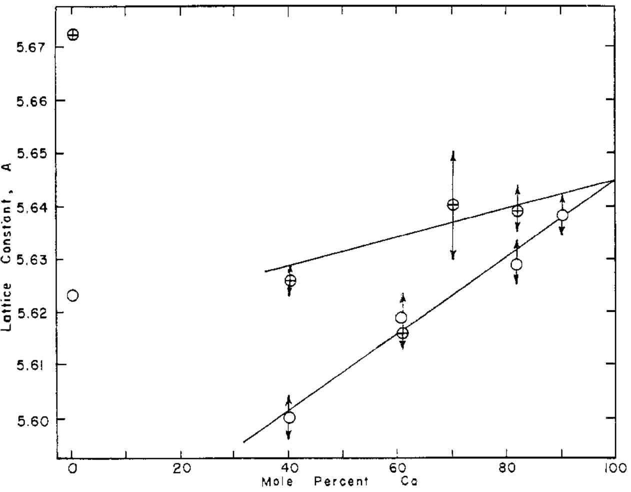

Figure 1.—Lattice constant *vs.* mole per cent calcium in metallic content, Ca–La–H samples: ○, series equilibrated at 400°; ⊕, series equilibrated at 700°.

Warf and Hardcastle[9] have demonstrated the existence of two face-centered-cubic forms of ytterbium hydride, prepared by allowing metal to react with H_2 at pressures above 1 atm. One of these has a composition of approximately $YbH_{2.5}$. The other, prepared by thermal decomposition of the first, is metastable at ordinary pressure and temperature in a sample of as low a hydrogen content as $YbH_{2.04}$.

In the process of adding hydrogen to YbH_2, conduction electrons would be released, and some Yb^{2+} would be changed to Yb^{3+}. The addition of lanthanum hydride to CaH_2 would produce La^{3+} and conduction electrons which might achieve the same effect. It should be noted that it is precisely the two rare earth dihydrides with few conduction electrons—YbH_2 and EuH_2—which are orthorhombic, while all others are cubic. The formation of the higher hydride of ytterbium indicates that the energy difference between the two structures may not be large, so that the conduction electrons or the additional lattice energy from the R^{3+} might produce the change.

It should be noted that CaH_2 undergoes a transition on heating at 780°,[10,11] to a phase of undetermined structure, possibly fcc.

Since the samples are not equilibrium samples, the possibility of no interaction must be examined. This would require that the observed fcc lattice constant would indicate how much of the total hydrogen was combined with La, the rest being combined with Ca. If this is done, using the closely agreeing lattice constants of Korst and Warf[12] and Goon,[13] the calculated compositions give the difficulty that, in most of the samples of Table I with less than two atoms of H per atom of La, there would be insufficient hydrogen to react with all of the Ca. There is no indication of uncombined Ca in the X-ray patterns, but again the amounts might be too small to detect.

Another assumption, in accord with the free energies of formation of CaH_2[11] and LaH_2,[12] would be that on combination hydrogen would first form LaH_2, then CaH_2. If any remained, it would react further with LaH_2. The number of gram-atoms of H combined with 1 g-atom of La, calculated in this way for each sample, does not correlate with the lattice constants of the fcc phase. There is a scattering of points, rather than the linear relationship of the literature results[12,13] in the absence of Ca. A lattice constant independent of the H to La ratio would again indicate a structural change in LaH_x caused by the presence of Ca.

No conclusions about the nature of the fcc phase in the Ca–La–H system may be drawn from this research, but interaction to form a novel phase is probable.

Acknowledgment.—This research was sponsored by the U. S. Atomic Energy Commission, Contract AT(30-1)1355.

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[10] D. T. Peterson and V. G. Fattore, *J. Phys. Chem.*, **65**, 2062 (1961).

[11] R. W. Curtis and P. Chiotti, *ibid.*, **67**, 1061 (1963).

[12] W. L. Korst and J. C. Warf, private communication.

[13] E. J. Goon, *J. Phys. Chem.*, **63**, 2018 (1959).

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The Thermal Decomposition of Copper(II) Chelates of N-Substituted Thiopicolinamides

BY RUDOLPH W. KLUIBER AND WILLIAM DEW. HORROCKS, JR.

Received February 3, 1966

In a previous study involving copper(II) chelates of N-substituted thiopicolinamides, the anomalous melting behavior of bis-(N-benzylthiopicolinamidato)-copper(II) (**1**) was observed.[1] This effect has now been more fully studied and found to involve the thermal reduction of the copper(II) chelate in part to the corresponding copper(I) chelate.

Experimental Section[2]

Thermal Decomposition of Bis-(N-benzylthiopicolinamidato)-copper(II).—Bis-(N-benzylthiopicolinamidato)copper(II) (0.211 g, 0.407 mmole, red-brown needles, mp 161° dec, $\mu = 1.83$ BM) was heated at 150° (0.2 mm) for 5 hr to yield a condensate of pure N-benzylthiopicolinamide (0.092 g, 0.403 mmole), identified by mixture melting point, infrared spectrum, and proton nmr spectrum, and a diamagnetic rust-colored residue (0.117 g, 99% of the residue expected, based on the loss of one molecule of N-benzylthiopicolinamide). Comparable results were observed for disproportionations carried out for varying times at temperature as low as 120°, although the residue obtained varied slightly from condition to condition. *Anal.* Calcd for $C_{13}H_{10}CuN_2S$: C, 53.87; H, 3.48; N, 9.67. Found: C, 53.85; H, 3.72; N, 9.70.

Prolonged (2 days) shaking of the residue in 6 *N* hydrochloric acid in the presence of air gave an insoluble green product which

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[1] R. W. Kluiber, *Inorg. Chem.*, **4**, 829 (1965). The melting point recorded for this complex is higher than that found in the present work and is attributed to the presence of two crystalline modifications.

[2] All temperatures are uncorrected. Nmr resonances are in ppm relative to tetramethylsilane as an internal standard, downfield being considered the negative direction.

was isolated by filtration, followed by washing with water and drying at 60° *in vacuo*. It contained a complex identical with one prepared by the addition of an excess of 12 *N* hydrochloric acid to bis-(N-benzylthiopicolinamidato)copper(II). After isolation by filtration, washing with water, and drying at 60° *in vacuo*, this complex showed in the infrared region an NH stretching frequency absorption at 3200 cm^{-1} and a very strong characteristic absorption at 1555 cm^{-1}. *Anal.* Calcd for $C_{13}H_{12}Cl_2CuN_2S$: C, 43.04; H, 3.33. Found: C, 43.11; H, 3.46.

Recovery of Organic Component from Decomposition Residue.—A mixture of 0.3 g of decomposition residue, 30 ml of water, 10 ml of concentrated sulfuric acid, and 30 ml of chloroform was stirred 27 hr (stirring up to 80 hr using even stronger acid gave approximately the same results). This mixture was diluted and extracted twice with 30-ml portions of chloroform. About half the acid was neutralized with sodium hydroxide and the solution was reextracted with several portions of chloroform. After drying, these extracts were concentrated to yield a chloroform-free oil. N-Benzylthiopicolinamide was recovered from this viscous oil. In addition to resonances attributable to this ligand, the nmr spectrum of the crude oil showed broad, nearly unresolved absorptions at about −8.1, −7.7, −7.4, −7.2, −6.55, −6.5 ppm having relative intensity 1:1:4:1:1:1.

Decomposition of Other N-Substituted Thiopicolinamide–Copper(II) Chelates.—Bis-(N-benzyl-4-methylthiopicolinamidato)copper(II), mp 153–155° dec, μ = 1.84 BM, was prepared from 4-methylthiopicolinamide, N-benzylamine, and copper sulfate in the usual manner.[1] *Anal.* Calcd for $C_{26}H_{26}CuN_4S_2$: C, 61.56; H, 4.79. Found: C, 61.74; H, 5.11. (The intermediate N-benzyl-4-methylthiopicolinamide was also isolated and characterized by its nmr spectrum; mp 77–78.5°, bp 185–190° (0.3 mm). *Anal.* Calcd for $C_{14}H_{14}N_2S$: C, 69.38; H, 5.82. Found: C, 69.19; H, 5.68.) Thermal degradation of this chelate (0.3 mm) at 150° (3 hr) resulted in a 51% weight loss, at 140° (16 hr) 54% loss, at 120° (48 hr) 53% loss, at 110° (105 hr) 48% loss (calculated weight loss for one molecule of N-benzyl-4-methylthiopicolinamide, 44.4%). The isolated volatile product in each case was N-benzyl-4-methylthiopicolinamide and the residue was diamagnetic.

Bis-(N-*n*-butylthiopicolinamidato)copper(II) (0.1489 g) lost 57.5 mg of N-*n*-butylthiopicolinamide (38.6%; weight loss calculated for the loss of one ligand, 43.2%) after heating for 24 hr at 150°. The residue did not contain N-*n*-butylthiopicolinamidatocopper(I) by comparison of its infrared spectrum with that of an authentic sample.

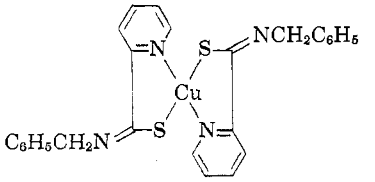
Bis-(N-*t*-butylthiopicolinamidato)copper(II) (350.2 mg) after 48 hr at 150° *in vacuo* lost 153.1 mg (43.7%). The recovered condensate, however, consisted of starting chelate as well as N-*t*-butylthiopicolinamide.

Borohydride Reduction of Copper(II) Chelates to Copper(I) Chelates.—To 1.4 g (2.7 mmoles) of bis-(N-benzylthiopicolinamidato)copper(II) in 50 ml of hot 1-propanol was added 0.5 g of potassium tetrahydridoborate (Alpha Inorganics), and the mixture was refluxed for 5–10 min. In this time an orange precipitate formed which was collected by filtration and washed successively with 1-propanol, water, 1-propanol, and petroleum ether (bp 40–60°). (N-Benzylthiopicolinamide was isolated from the filtrate.) The yield of diamagnetic product after drying at 80° was 0.65 g (89%). *Anal.* Calcd for $C_{13}H_{11}N_2SCu$: C, 53.68; H 3.81; N, 9.63. Found: C, 54.06; H, 4.17; N, 9.67.

In a similar manner N-*n*-butylthiopicolinamidatocopper(I) was prepared from bis-(N-*n*-butylthiopicolinamidato)copper(II). The infrared spectrum of this diamagnetic chelate has its strongest absorption at 1575 cm^{-1}. *Anal.* Calcd for $C_{10}H_{13}CuN_2S$: C, 46.76; H, 5.10; N, 10.91. Found: C, 46.43; H, 5.35; N, 10.75.

Results and Discussion

At elevated temperatures (100–200°) bis-(N-benzylthiopicolinamidato)copper(II) (**1**) decomposes to yield one molecule of N-benzylthiopicolinamide (**2**) and an orange- to rust-colored residue about half of which is N-benzylthiopicolinamidatocopper(I) (**3**). This residue is diamagnetic, supporting formulation as a d^{10} complex although not ruling out the presence of strongly antiferromagnetic compounds such as copper sulfide.



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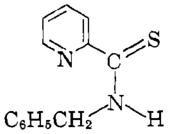

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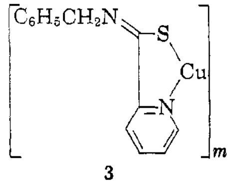

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However, a solution of the residue in hydrochloric acid is slowly air oxidized, substantiating the copper(I) assignment. This oxidation product was shown by its infrared spectrum and powder X-ray diffraction pattern to contain substantial amounts of a 1:1 N-benzylthiopicolinamide:copper(II) chloride complex, alternately synthesized by the reaction of **1** with hydrochloric acid or by the addition of N-benzylthiopicolinamide to cupric chloride. Other examples of such 1:1 complexes have been previously reported.[3] Evidence for the presence of N-benzylthiopicolinamidatocopper(I) (**3**) in the residue product was obtained by the synthesis of an authentic sample of this chelate by borohydride reduction of the cupric chelate (**1**). A comparison of its infrared spectrum with that of the thermal decomposition residue confirmed the presence of **3** in the residue.

Additional information on the nature of the decomposition residue was obtained by recovery of the organic ligand by oxidative hydrolysis. Analysis by nmr indicates that about 50 mole % of the organic residue is N-benzylthiopicolinamide (**2**). The remainder contains approximately two less protons per pyridine unit and is probably polymeric, as evidenced by the broadness of the nmr resonances and the viscous nature of the crude recovered organic products. Such results are in agreement with the hydrogen stoichiometry required by the decomposition. Assuming no rearrangement of the organic ligand during the hydrolysis, the absence of benzylic resonances and proton resonances below −8.2 ppm in the polymeric product suggests it to be formed by the removal of a benzylic hydrogen and substitution of the pyridine ring. The loss of a benzylic proton is supported qualitatively by infrared spectra, which show a diminution in the intensity of the benzyl CH_2 stretching frequency at 2880 cm^{-1} relative to the aromatic protons in the residue product in comparison with an authentic sample of **3**. The absence of an infrared absorption between 800 and 850 cm^{-1} and the presence of new peaks at

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[3] J. L. Rainey and R. C. Mansfield, U. S. Patent 2,938,907 (1960); *Chem. Abstr.*, **54**, 19720 (1960).

761 and 689 cm^{-1} in the recovered ligand and the residual product coupled with the nmr data support substitution of the pyridine ring at the 3 or 6 position in the polymeric organic portion of the residue.

The thermal decomposition of bis-(N-alkylthiopicolinamidato)copper(II) complexes to produce cuprous compounds and protonated ligand appears to be a general reaction though not necessarily one of simple stoichiometry. That this disproportionation is facilitated by the presence of reactive protons on the carbon adjacent to the amide nitrogen is supported by the slow thermal degradation of bis-(N-*t*-butylthiopicolinamidato)copper(II) and the reported stability of the N-phenyl copper(II) chelate.[4] Facile and specific removal of similarly situated protons has been noted for radical reactions with amines,[5] as well as in the reduction of cupric chloride by amines.[6] The particular reactivity of benzylic protons is demonstrated by the reported conversion of toluene to bibenzyl in the presence of cupric chloride.[7] The loss of aromatic protons in reactions involving cupric compounds has recently been reviewed.[8] The present decomposition can also be compared with the thermal decompositions of copper acetylacetonate[9] and copper benzoate.[10] In these examples a principal degradation product is the protonated ligand. In close analogy with the present work cuprous benzoate and aromatic substituted products were reported in the thermal degradation of copper benzoate.[10] In the present systems isolation of the cuprous chelate may be further facilitated by the π-electron acceptor and the multiple coordination characteristics of the sulfur atom.

Acknowledgment.—Support of this research by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, through Contract No. AF 49(638)-1492 is gratefully acknowledged.

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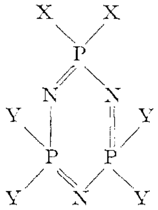
Bis(arylamino)tetrachlorophosphonitriles and Bis(arylamino)tetrakis(polyfluoroalkoxy)phosphonitriles[1]

BY HENRY LEDERLE, GERHARD OTTMANN, AND EHRENFRIED KOBER

Received February 4, 1966

Although arylamino-disubstituted tetrameric phosphonitrilic chlorides, $P_4N_4Cl_6(NHaryl)_2$, have been described,[2] previous attempts to synthesize arylamino-disubstituted trimeric phosphonitrilic chlorides, $P_3N_3Cl_4(NHaryl)_2$, have met with failure.[3] We now wish to report that we have synthesized 2,2-bis(anilino)-4,4,6,6-tetrachlorophosphonitrile (I), mp 207.5–208.5°, in 30% yield from $(PNCl_2)_3$ and 2 moles of aniline in presence of triethylamine and in toluene as solvent. Because of its low solubility in toluene, relative to the other components of the reaction mixture, compound I precipitates together with triethylamine hydrochloride, from which it is separated by extraction with boiling toluene. Phosphorus-31 nuclear resonance spectroscopy confirms structure I. On irradiation of ^1H at 47.6 MHz the ^{31}P spectrum appears as an AB_2 spectrum with a coupling constant of 48 Hz. The doublet of relative intensity 2 at 20.4 ppm is indicative of a phosphorus atom bonded to two chlorine atoms. The triplet of unit relative intensity at 2.3 ppm is consistent with a symmetrical arrangement of the attributed phosphorus atom between two of the other type.



I–V

I: $X = C_6H_5NH$
$Y = Cl$

II: $X = C_6H_5NH$
$Y = CF_3CH_2O$

III: $X = C_6H_5NH$
$Y = CHF_2CF_2CH_2O$

IV: $X = m\text{-}ClC_6H_4NH$
$Y = Cl$

V: $X = m\text{-}ClC_6H_4NH$
$Y = CF_3CH_2O$

Structure I confirms a geminal substitution pattern for the replacement of the chlorine atoms of $(PNCl_2)_3$ by aromatic amino groups.[3] The isolation of compound I gives some support to a possible structure of the transition state of this reaction suggested on the basis of kinetic measurements.[4] In this connection, it should be noted that substitution of two chlorine atoms by anilino groups in the tetrameric series apparently does not proceed by a geminal pattern but yields 2,6-bis(anilino)-2,4,4,6,8,8-hexachlorophosphonitrile.[2]

Reactions of compound I with sodium trifluoroethoxide and sodium tetrafluoropropoxide afforded 2,2-bis(anilino)-4,4,6,6-tetrakis(2,2,2-trifluoroethoxy)phosphonitrile (II) and 2,2-bis(anilino)-4,4,6,6-tetrakis(2,2,3,3-tetrafluoropropoxy)phosphonitrile (III), respectively. Confirmation of these structures by nmr spectroscopy was sought in case of II. The ^1H spectrum, which shows an aromatic resonance of relative intensity 5 centered at 7.11 ppm, an N–H resonance of relative intensity 1 at 5.20 ppm, and a third multiplet of relative intensity 4 at 4.14 ppm, indicates a 2:1 ratio of fluoroalkoxy groups to anilino groups. The decoupled ^{31}P spectrum[5] shows an AB_2 pattern

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(1) This work was supported by the Bureau of Ships, U. S. Navy, under Contract NObs 90092.

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