

Complex Metal-Nicotine Compounds

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This work is a continuation of the efforts of this Laboratory to prepare a large number of derivatives and compounds of nicotine.^{1,2} In one pre-

vious publication³ 25 complex salts of nicotine, some involving acid dyes, were listed but not described. In another⁴ the author described the preparation of 11 double sulfates. The present paper covers the preparation of 76 complex metal-nicotine compounds of two types—double salts and nicotinammino compounds.

TABLE I
THIOCYANATES

No.	Compound ^a	Nicotine, %		-CNS, %		Crystals
		Calcd.	Found	Calcd.	Found	
1	ZnA ₂ ·RN ₂ ·HA	40.2	40.2	43.2	42.9	Dimorphic, irregular or prisms
2	CdA ₂ ·2(RN ₂ ·HA)	48.3	48.3	34.6	34.6	Irregular leaves
3	CdA ₂ ·2RN ₂	58.6	59.7	21.0	21.3	Prisms (tricl.), often in rosettes
4	CoA ₂ ·2(RN ₂ ·HA)	52.5	52.5	37.6	37.7	Red prisms (tricl.)
5	NiA ₂ ·2(RN ₂ ·HA)	52.5	52.4	37.6	37.1	Blue-green prisms (tricl.)
6	NiA ₂ ·3RN ₂	73.5	72.3	17.6	17.2	Brown, irregular
7	MnA ₂ ·2(RN ₂ ·HA)	52.8	52.1	37.9	36.9	Prisms
8	FeA ₂ ·2(RN ₂ ·HA)	52.8	52.4	37.8	37.7	Yellow prisms (tricl.)
9	3AgA·RN ₂ ·HA	22.5	22.6	(8.0) ^b	(8.0) ^b	Pink prismatic needles, m.p. 130–131°
10 ^c	CuA ₂ ·2(RN ₂ ·HA)	52.1	50.0	Irregular green
11 ^c	CuA·RN ₂ ·HA	47.3	47.2	Irregular yellow
12 ^c	CuA·RN ₂	57.1	55.6	Rod-like prisms
13 ^d	CrA ₃ ·1.3(RN ₂)·4H ₂ O	41.4	40.8	34.2	34.0	Purple, irregular
Piperidine, %						
14	CoA ₂ ·2(C ₅ H ₁₁ N·HA)	36.7	37.2	50.1	50.0	Deep-blue prisms

^a A = -CNS; RN₂ = C₁₀H₁₄N₂. ^b Refers to -CNS combined with nicotine, determined by warming the compound in water acidified with nitric acid, cooling, and titrating. ^c No. 10, 11 and 12: calcd., Cu 10.2, 18.5 and 22.9, respectively; found, Cu, 10.9, 18.4 and 22.5, respectively. ^d Calcd., Cr, 10.2; found, Cr, 9.9.

TABLE II
SALICYLATES

No.	Compound ^a	Nicotine, %		Salicylic acid, %		Crystals
		Calcd.	Found	Calcd.	Found	
1	CuA ₂ ·2(RN ₂ ·HA)	34.6	34.6	Purple prisms
2	CuA ₂ ·2(RN ₂ ·HA)·H ₂ O	34.3	34.3	56.7	57.1	Blue prisms
3	CoA ₂ ·2(RN ₂ ·HA)·2H ₂ O	33.5	33.6	56.8	56.2	Pink plates, irregular
4	MnA ₂ ·2(RN ₂ ·HA)·2H ₂ O	33.6	33.6	57.2	56.8	Irregular
5	CdA ₂ ·2(RN ₂ ·HA)·2H ₂ O	31.7	31.5	54.4	54.4	Irregular
6	ZnA ₂ ·2(RN ₂ ·HA)·2H ₂ O	33.3	33.4	56.7	56.4	Irregular
7	NiA ₂ ·2(RN ₂ ·HA)·2H ₂ O	33.4	33.1	56.8	56.4	Irregular

^a A = -OOC(C₆H₄)OH-*o*; RN₂ = C₁₀H₁₄N₂.

TABLE III
PICRATES

No.	Compound ^a	Nicotine, %		Picric acid, %		H ₂ O, %	Loss at 110°, %	
		Calcd.	Found	Calcd.	Found		15 min.	30 min.
1	CoA ₂ ·2RN ₂ ·5H ₂ O	34.9	34.9	48.9	48.3	9.7	9.8	9.8
2	NiA ₂ ·2RN ₂ ·6H ₂ O	34.3	34.1	48.4	48.9	11.4	11.4	11.4
3	CdA ₂ ·2RN ₂ ·6H ₂ O	32.4	32.4	45.8	46.1	10.8	7.6	7.9
4	MgA ₂ ·2RN ₂ ·6H ₂ O	35.5	35.4	50.2	51.1	11.8	11.5	12.7
5	MnA ₂ ·2RN ₂ ·4H ₂ O	35.7	35.7	50.5	51.1	7.3	7.3	7.9
6	ZnA ₂ ·2RN ₂	38.3	38.3	54.2	54.7
7	AlA ₃ ·3RN ₂	40.6	40.5	57.4	57.8
8	FeA ₃ ·3RN ₂	39.7	39.7	56.0	56.2
9	AgA·RN ₂	32.6	33.3	46.0	45.8
10 ^b	CuA ₂ ·2(RN ₂ ·HA)	24.9	25.2
11	ZnA ₂ ·2(RN ₂ ·HA)	24.8	24.3
12 ^c	AgA·2(RN ₂ ·HA)	29.0	29.1

^a A = -OC₆H₂(NO₂)₃; RN₂ = C₁₀H₁₄N₂. ^b Calcd., Cu, 4.9; found, Cu, 5.1. ^c Calcd., Ag, 9.6; found, Ag, 9.0.

(1) C. F. Woodward, A. Eisner and P. G. Haines, *THIS JOURNAL*, **66**, 911 (1944); P. G. Haines, A. Eisner and C. F. Woodward, *ibid.*, **67**, 1258 (1945); P. G. Haines and A. Eisner, *ibid.*, **72**, 4618, 1719 (1950).
(2) C. F. Woodward, C. O. Badgett and J. J. Willaman, *Ind. Eng. Chem.*, **36**, 540, 544 (1944); U. S. Dept. Agric. E-725 (processed) (1917); *Arch. Biochem.*, **29**, 241 (1950).

Double salts result from the combination of the metal and the nicotine salts of the same selected acid. Anunino compounds result when nicotine

(3) C. R. Smith, U. S. Dept. Agric. E-646 (processed) (1945).
(4) C. R. Smith, *THIS JOURNAL*, **71**, 2844 (1949).

TABLE IV

<i>o</i> -BENZOYL BENZOATES								
No.	Compound ^a	Nicotine, %		HA, %		H ₂ O, %	Loss at 110°, %	
		Calcd.	Found	Calcd.	Found	Calcd.	15 min.	30 min.
1	CoA ₂ ·2RN ₂ ·6H ₂ O	34.5	34.4	48.0	48.5	11.4	9.9	10.6
2	NiA ₂ ·2RN ₂ ·6H ₂ O	34.5	34.3	48.1	47.8	11.4	10.1	10.1
3	MnA ₂ ·2RN ₂ ·6H ₂ O	34.6	34.5	48.2	48.6	11.5	9.7	11.0
4	CdA ₂ ·2RN ₂ ·6H ₂ O	32.5	32.6	45.4	45.2	10.8	10.0	10.6
5	ZnA ₂ ·2RN ₂ ·6H ₂ O	34.2	34.0	47.7	48.3	11.4	8.8	9.9
6	MgA ₂ ·2RN ₂ ·6H ₂ O	35.8	35.9	49.9	49.8	11.9	11.8	13.6
7	FeA ₂ ·2RN ₂ ·6H ₂ O	34.6	34.4	48.2	48.4	11.5	9.4	9.9
8 ^b	CuA ₂ ·2RN ₂ ·5H ₂ O	35.0	35.0	9.7	9.3	9.4
9 ^b	CuA ₂ ·2RN ₂ ·2C ₂ H ₅ OH	34.8	34.8	(9.9) ^c	9.6	10.5
10 ^d	(AgA) ₂ ·RN ₂	19.6	20.6
11 ^b	CuA ₂ ·2(RN ₂ ·HA)	25.0	24.2

^a A = OOC·C₆H₄(OC·C₆H₅)_o; RN₂ = C₁₀H₁₄N₂. ^b No. 8, 9 and 12: calcd., Cu, 6.8, 6.8 and 4.8, respectively; found, Cu, 6.8, 6.8 and 4.6, respectively. ^c Ethanol. ^d Calcd., Ag, 26.1; found, Ag, 26.0.

TABLE V

<i>p</i> -NITROBENZOATES								
No.	Compound ^a	Nicotine, %		HA, %		H ₂ O, %	Loss at 110°, %	
		Calcd.	Found	Calcd.	Found	Calcd.	15 min.	30 min.
1	CoA ₂ ·2RN ₂ ·4H ₂ O	41.1	40.7	42.4	42.6	9.1	8.2	8.2
2	CdA ₂ ·2RN ₂ ·4H ₂ O	38.5	38.3	39.7	39.7	8.6	9.1	9.3
3	MnA ₂ ·2RN ₂ ·4H ₂ O	41.4	40.9	42.6	42.9	9.2	9.1	10.9
4	CuA ₂ ·2RN ₂ ·2H ₂ O	42.8	42.9	44.2	44.5	4.8	4.8	4.8
5	NiA ₂ ·2RN ₂ ·2H ₂ O	43.1	42.0	44.5	44.8	4.7	4.1	4.1
6 ^b	CuA ₂ ·2RN ₂ ·4HA	23.4	23.3

^a A = -OCC·C₆H₄·NO-*p*; RN₂ = C₁₀H₁₄N₂. ^b No. 7: calcd., Cu, 4.6; found, Cu, 4.6.

TABLE VI

DIBASIC ACIDS						
No.	Compound ^a	Base, %		Copper, %		Crystals
		Calcd.	Found	Calcd.	Found	
1 ^b	CuC ₂ O ₄ ·Na ₂ C ₂ O ₄ ·2H ₂ O	19.8	19.6	Blue prismatic needles
2	CuC ₂ O ₄ ·RN ₂ ·H ₂ C ₂ O ₄	40.1	39.3	15.7	15.7	Blue prisms (moncl.)
3	CuC ₂ O ₄ ·RN ₂ ·H ₂ C ₂ O ₄ ·H ₂ O	38.4	38.7	14.9	14.8	Prisms, round ends
4 ^c	2CoC ₂ O ₄ ·RN ₂ ·H ₂ C ₂ O ₄ ·5H ₂ O	25.5	24.7
5 ^d	2ZnC ₂ O ₄ ·RN ₂ ·H ₂ C ₂ O ₄ ·5H ₂ O	25.5	25.0
6	CuPhth·RN ₂ ·H ₂ Phth·H ₂ O	28.3	28.2	11.1	11.1	Green, irreg.
7	CuPhth·2HN ₃	13.0	12.9	24.3	24.2	Blue prisms (tetrag.)
8	CuCr ₂ O ₇ ·2RN ₂ ·H ₂ Cr ₂ O ₇	39.5	39.3	7.7	7.6	Brown to orange, irreg.
9	CdCr ₂ O ₇ ·2RN ₂ ·H ₂ Cr ₂ O ₇	37.2	36.0	Salmon to brown
10	Cu(OOC·CH ₂) ₂ ·RN ₂	47.4	42.9	19.6	18.0	Green cubes
11	Cu(OOC·CH ₂) ₂ ·2NH ₃ ·2H ₂ O	13.6	13.9	25.4	25.3	Purple prisms (tricl.)
12	Cu(OOC·CH ₂) ₂ ·2NH ₃	15.9	15.5	29.7	29.3	Blue prisms (tetrag.)
13	Cu(OOC=CH) ₂ ·2RN ₂ ·10H ₂ O	47.5	47.3	9.3	9.3	Blue prisms (tricl.)
14 ^e	ZnC ₂ O ₄ ·NH ₃ ·3H ₂ O	7.6	7.2	White prisms

^a RN₂ = C₁₀H₁₄N₂; Phth = -(OOC)₂C₆H₄-*o*. ^b Calcd.: H₂C₂O₄, 78.4; H₂O, 24.0. Found: H₂C₂O₄, 79.0; H₂O loss at 110°, 22.6. ^c Calcd.: H₂C₂O₄, 42.5; H₂O, 14.1. Found: H₂C₂O₄, 42.8; H₂O loss at 110°, 13.7. ^d Calcd.: H₂C₂O₄, 42.5; H₂O, 14.1. Found: H₂C₂O₄, 42.5; H₂O loss at 110°, 14.0. ^e Calcd.: H₂C₂O₄, 39.2; H₂O, 24.0. Found: H₂C₂O₄, 39.0; H₂O loss at 110°, 22.6.

alkaloid reacts with a metal salt of the selected acid. The metals which made double salts were Ag, Cd, Co, Cu (-ous and -ic), Fe (-ous and -ic), Mn (-ous) and Ni (-ous). All of these, plus Al, Cr and Mg, formed ammino compounds. The acids successfully incorporated into double salts were benzoic, *o*-benzoylbenzoic, *p*-nitrobenzoic, chromic, hydrocyanic, oxalic, phthalic, picric, salicylic and thiocyanic. Those in ammino compounds were benzoic, *o*-benzoylbenzoic, *p*-nitrobenzoic, ferrocyanic, fumaric (but not maleic), hydrobromic, hydriodic, α -naphthoic, phthalic, picric, succinic and thiocyanic.

Univalent cations combined with univalent anions added only 1 mole of base, forming a mononicotinammino product. Bivalent cations combined

with univalent anions formed dinicotinammines, and trivalent cations combined with univalent

TABLE VII

BENZOATES AND NAPHTHOATE						
No.	Compound ^a	Nicotine, %		Metal, %		Crystals
		Calcd.	Found	Calcd.	Found	
1	CuA ₂ ·2(RN ₂ ·HA)	37.1	35.9	7.3	7.5	Blue prisms
2	CuA ₂ ·2RN ₂ ·2H ₂ O	48.7	48.6	9.6	9.8	Blue prisms
3	CuA ₂ ·RN ₂	34.4	34.0	13.6	13.4	Green hex. plates
4	CoA ₂ ·2(RN ₂ ·HA) ^b	37.3	35.6
5	NiA ₂ ·2(RN ₂ ·HA) ^c	37.3	33.4
6	ZnA ₂ ·RN ₂ ·HA	27.3	27.4
7	CdA ₂ ·2RN ₂	47.7	46.2	Plates
8	CuN ₂ ·2RN ₂ ^d	44.4	44.4	8.7	8.8	..

^a A = -OOC·C₆H₅; RN₂ = C₁₀H₁₄N₂. ^b Calcd., C₆H₅·CO₂H, 56.1; found, C₆H₅·CO₂H, 53.4. ^c Calcd., C₆H₅·CO₂H, 56.2; found, C₆H₅·CO₂H, 54.3. ^d N = -OOC₁₀H₇- α .

TABLE VIII
 HALIDES, CYANIDES AND FERROCYNANIDES

No.	Compound ^a	Nicotine, %		Copper, %		Crystals
		Calcd.	Found	Calcd.	Found	
1	2CuCN·RN ₂ ·HCN	44.0	43.0	34.5	34.2	Prisms (tricl.)
2	CuI·RN ₂	46.0	43.2	Hydrous, irregular
3 ^b	Ag ₂ ·RN ₂ ·H ₂ FeCy ₂ 2H ₂ O	25.9	25.9			

^a RN₂ = C₁₀H₁₄N₂. ^b Calcd., Ag, 34.2; found, Ag, 34.8.

anions formed trinicotinamines; nickelous trinicotinamino thiocyanate was an exception. Bivalent cations (principally limited to copper) combined with bivalent anions usually added 2 moles of ammonia or 1 mole of nicotine; the nicotine double salts usually contained only 1 mole of nicotine, but cupric dinicotine dichromate was an exception. The author prepared only two trinicotinamines of trivalent cations—the trinicotinamino picrates of aluminum and iron. Bivalent cations were often associated with 2 moles of nicotine and up to 6 moles of water.

In general, both types of salts were well crystallized, highly water-insoluble compounds of definite and repeatable composition. Many of them contained definite amounts of water of crystallization; in others this was indefinite or fluctuating. Usually they could be prepared by mixing normal solutions of the required salts in water or in water-ethanol, using the acetates of the desired metals and the sodium or ammonium salts of the desired anions. Manipulations had to be juggled in some cases to avoid the formation of metal hydroxides, or to produce the latter in finely dispersed and reactive form. Sometimes one listed compound was prepared from another, as in Table VI, no. 3 from no. 2; and in Table VII, 3 from 2. Usually the crystals formed immediately, sometimes after a few days at room temperature.

Many of the compounds fluoresced. Some of these were cuprous nicotine thiocyanate (Table I), the cadmium salts of nicotine salicylate (Table II) and thiocyanate, and the zinc salts of nicotine thiocyanate, salicylate and benzoate (Table VII).

In the tables, RN₂ is used as an abbreviation for nicotine, C₁₀H₁₄N₂, where R represents C₁₀H₁₄, obviously not a definite radical, and N₂ indicates possible chelation of two nitrogens.

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Theory of the Variation of Bond Length with Bond Environment

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Recently a theory of the distribution of electronic charge in aliphatic organic molecules has been published.² This theory is particularly useful for calculating the variation of the moment of a C-X (X = halogen or hydrogen) bond with the environ-

ment of the bond. Concurrently with the development of this theory and its successful application to several problems, a number of C-X internuclear distances ("bond lengths") in substituted methanes have been accurately determined with the use of microwave spectroscopy. In this paper we propose to show that most of the bond length variations with environment which are observed may be related quantitatively to the bond moment variations calculated with inductive effect theory.

Our theory of bond length variation in saturated molecules is based on the model used in discussing charge distributions.³ This model has a molecule consisting of touching spheres, each sphere representing an atom and having a radius equal to the covalent bond radius. Spread out over the surface of the sphere representing atom *a* is an amount of electronic charge equal to the "net charge," ϵ_a , which atom *a* carries. This net charge "sees" charge Z_a , the effective nuclear charge of atom *a*, given by

$$Z_a = Z_a^\circ + s_a(\epsilon_a/e) \quad (1)$$

where e is the negative of the charge of an electron, Z_a° is the effective nuclear charge of atom *a* when it carries zero net charge, and s_a is 0.30 or 0.35 accordingly as *a* is or is not hydrogen. Equation (1) is an interpolation of one of Slater's screening rules.^{2,3}

Let us now consider an equation holding for Slater approximate atomic orbitals,³ namely

$$R_a = ((n_a^*)^2/Z_a)a_0 \quad (2)$$

where a_0 = Bohr radius = 0.53 Å., n_a^* is the "effective quantum number" for atom *a*, and R_a is the distance from the nucleus for which the electronic density for the shell under consideration is a maximum, and may be considered to be the radius of the atom. From equation (2) we see that, for a given effective quantum number (electron shell), an increase in effective nuclear charge goes along with a decrease in effective radius, and *vice versa*. This may be pictured as a "pulling in" of the electron shell by the increased positive effective nuclear charge.

If we consider molecules from the atomic orbital point of view, which is essentially what we are doing when we use the charged sphere model under discussion, we may expect that equation (2) may have a degree of applicability to molecules; just what this degree is cannot be given a clear-cut theoretical answer, but it must be determined empirically. Let us make the following supposition, to be tested empirically. We suppose that equation (2), when coupled with equation (1), may satisfactorily be used for discussing the variation of the effective radius of an atom in a

(1) Junior Fellow, Harvard Society of Fellows, 1951-.

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