

A variety of experiments may shed light on the nature of these "pseudo-superoxides." These experiments will, however, involve a considerable length of time so we feel that the observation on the magnetism should be reported at this time.

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### The Structure of Five-Coordinated High-Spin Complexes of Nickel(II) and Cobalt(II) with N-β-Diethylamineethyl-5-chlorosalicylaldehyde<sup>1</sup>

Sir:

Ring-substituted salicylaldehydes form with N,N-diethylethylenediamine Schiff bases of the general formula  $XC_6H_3(OH)CH=NC_2H_4N(C_2H_5)_2$ . These ligands give complexes with nickel(II) of the general formula  $[X-SALen-N(C_2H_5)_2]_2Ni$ . Paramagnetic octahedral or diamagnetic planar complexes are formed depending on the nature of the X substituent in the benzene ring. When X = 3-Cl, 5-Cl, or 3,4-benzo, paramagnetic compounds ( $\mu_{eff} = 3.3$  B.M.) of indeterminate structure are formed. Their reflectance spectra differ from those of the octahedral and planar forms. In solution, the absorption spectra show the existence of octahedral, planar, and unknown species.<sup>2</sup>

$[5-Cl-SALen-N(C_2H_5)_2]_2Ni$  and also  $[5-Cl-SALen-N(C_2H_5)_2]_2Co$  are isomorphous with the following crystal data, respectively:  $a = 12.68, 13.20$  Å.;  $b = 21.77, 21.86$  Å.;  $c = 12.05, 12.15$  Å.;  $\beta = 122^\circ 48', 126^\circ 25'$ ;  $Z = 4$ ;  $d_c = 1.32, 1.31$  g./cm.;  $V_M = 699.4, 705.4$  Å.; space group  $P2_1/c$ .

Three-dimensional data have been collected on the nickel complex by the equi-inclination Weissenberg technique using Cu  $K\alpha$  radiation. The structure has been solved by three-dimensional Patterson and Fourier syntheses and refined by several cycles of least squares.

- (1) Supported by the Italian Consiglio Nazionale delle Ricerche.  
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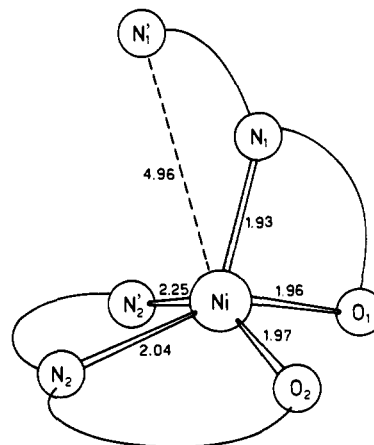


Figure 1. Sketch of the molecular structure of  $[5-Cl-SALen-N(C_2H_5)_2]_2Ni$ . Salicylaldimines residues are schematically represented by full lines.

At the present stage of refinement  $R$  is 0.15 over 1033 observed, independent reflections.

The structure consists of discrete molecules in which nickel(II) has a coordination number of five. The coordination polyhedron can be described as a distorted square pyramid (Figure 1). Bond lengths about the nickel atom are shown in the figure. The angles are:  $O_1-Ni-O_2 = 94^\circ$ ,  $O_2-Ni-N_2 = 89^\circ$ ,  $N_2-Ni-N_2' = 80^\circ$ ,  $N_2'-Ni-O_1 = 90^\circ$ ,  $O_1-Ni-N_1 = 92^\circ$ ,  $O_2-Ni-N_1 = 100^\circ$ ,  $N_2-Ni-N_1 = 105^\circ$ ,  $N_2'-Ni-N_1 = 105^\circ$ . The basal set of four ligands lies in a plane within 0.1 Å. The nickel atom is 0.36 Å. above this plane. The nickel to nonbonded nitrogen atom distance is 4.96 Å. The shortest intermolecular nickel to nonbonded nitrogen distance is 7.81 Å.

This structure represents the first example of a high spin nickel(II) complex so far described with a five-coordinate geometry.

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### The Structure of Villalstonine<sup>1</sup>

Sir:

Alkaloid B (m.p. 235–270 dec. (*in vacuo*),  $[\alpha]^{25D} + 79^\circ$  ( $c$  1.0, pyridine)) isolated from *Alstonia muelleriana* Domin by Elderfield and co-workers<sup>2</sup> was characterized by them as an indole alkaloid of approximate composition  $C_{40}H_{50}O_4N_4$ . A tentative identification<sup>3</sup> of Alkaloid B with villalstonine<sup>4</sup> has been confirmed by a comparison of single crystal X-ray diffraction patterns.<sup>5</sup> We wish to report the result of a crystallographic study which establishes the molecular structure

(1) This investigation was supported by Public Health Service Research Grants HE 04179 and HE 08612 from the National Heart Institute.

(2) R. C. Elderfield, R. E. Gilman, and A. Okano, to be published; R. E. Gilman, Ph.D. Thesis, University of Michigan, 1959.

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(5) We are grateful to Dr. A. Chatterjee for sending us a sample of authentic villalstonine.

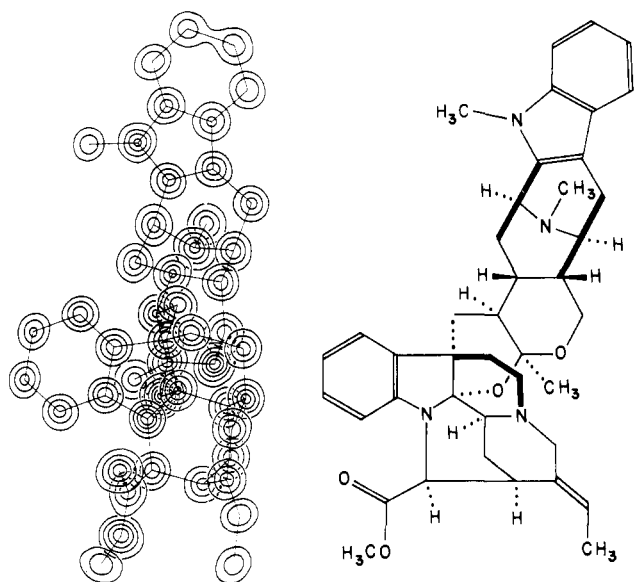


Figure 1. Electron density in the villalstonine molecule, contoured at 2, 4, 6, ... e. Å.<sup>-3</sup>, and a schematic structural formula.

of villalstonine and confirms the recently revised<sup>6</sup> empirical formula as C<sub>41</sub>H<sub>48</sub>O<sub>4</sub>N<sub>4</sub>.

Crystals of villalstonine from methanol solution are monoclinic and belong to space group P2<sub>1</sub>. The unit cell of dimensions  $a = 13.756 \text{ \AA}$ ,  $b = 13.645 \text{ \AA}$ ,  $c = 10.045 \text{ \AA}$ , and  $\beta = 101^\circ 41'$  contains two molecules of the alkaloid and two molecules of methanol. The Patterson function was calculated using 3337 observed, independent X-ray intensities, densitometrically evaluated from integrated oscillation photographs. The solution of the structure made use of the known presence in the molecule of a rigid group of 11 atoms in known configuration, namely an indole group and two adjacent carbon atoms. Rotational and translational searches<sup>7</sup> of the Patterson function yielded several plausible positions for the two symmetry-related (2<sub>1</sub>) rigid groups in the unit cell. A vector-space refinement procedure was employed in making a choice among these possibilities. This procedure, programmed for the IBM 7090, refines the atomic coordinates of a partially known crystal structure by optimizing the fit of the interatomic vectors to the stored, three-dimensional Patterson function. The best-fitting set of refined atom coordinates was then used as the basis for a 22-fold Patterson superposition, which yielded the positions of most of the remaining atoms. Difference Fourier syntheses and least-squares refinement ultimately established the complete structure, with  $R = 0.059$  for the observed reflections.

The structure and relative configuration of villalstonine are shown in Figure 1. The lower part of the figure matches the structure of pleiocarpamine,<sup>8</sup> confirming the observation<sup>9</sup> that the latter alkaloid is a product of the acid-catalyzed fission of villalstonine.

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The other half of the villalstonine molecule does not appear to correspond to any alkaloid whose structure is known at the present time. However, the skeleton of this half is closely related to that of Alkaloid C,<sup>2,7</sup> an oxindole alkaloid from the same source, *A. muelleriana*.

The absolute configuration of villalstonine is probably that of Figure 1, which is based on the probable absolute configuration of pleiocarpamine,<sup>8</sup> which in turn is based on the rule of uniform absolute stereochemistry at C-15 of yohimbinoid alkaloids.<sup>10</sup> In this connection it should be noted that the previously published configuration<sup>7</sup> for Alkaloid C, which was supposed to have conformed to the C-15 rule,<sup>10</sup> was in actual fact the mirror image of what had been intended.

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### Nuclear Magnetic Resonance Spectra (200 Mc.p.s.) of the Aromatic Protons of Alkylbenzenes and Biphenyl

Sir:

Despite extensive investigation of the effect of a variety of substituents on the n.m.r. spectral parameters of benzene ring protons,<sup>1-13</sup> very little is known concerning the effect of alkyl groups alone. Monosubstituted benzenes give complex aromatic spectra arising from five strongly coupled spins; in alkylbenzene spectra this difficulty is aggravated by the very small chemical shift differences among these protons. Despite their forbidding appearance, however, the 60 Mc.p.s. spectra of certain alkylbenzenes suggested that analyzable spectra might be obtained at frequencies of the order of 200 Mc.p.s. This communication describes the results of such a study.

The spectrometer was an experimental instrument developed by Varian Associates and described by Nelson and Weaver.<sup>14</sup> It employs a 47 kgauss superconducting solenoid, corresponding to a 200 Mc.p.s. radiofrequency field for protons. Resolution was 1.0-1.2 c.p.s. Sensitivity being somewhat below that of present commercial instruments, neat liquids or 25% (v./v.) solutions in CCl<sub>4</sub> were used.<sup>15</sup> Spectra

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(15) Isotactic polystyrene, included in Figure 1 and Table I for comparison, was run in tetrachloroethylene solution at 128° using a Varian DP-60 instrument. Because of unusual shielding effects, the 60 Mc.p.s. spectrum was analyzable.