The Crystal and Molecular Structure of Dichlorobis-(4-vinylpyridine)cobalt(II)

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SOLID-STATE POLYMERIZATION is known to be strongly dependent on the structural arrangement of the molecules involved. Structural information has therefore been obtained on dichloro-4-vinylpyridine complexes to aid understanding of their polymerization with temperature.

The dark blue crystals of $Co(NC_5H_4{\cdot}C_2H_3)_2Cl_2$ are monoclinic; $a = 20{\cdot}20 \pm 0{\cdot}04$, $b = 6{\cdot}47 \pm 0{\cdot}02$, $c = 14{\cdot}61 \pm 0{\cdot}04$ Å, $\beta = 126 \pm 0{\cdot}5°$, $Z = 4$, $D_c = 1{\cdot}47$, $D_m = 1{\cdot}46$. The trial structure followed from a Patterson synthesis based on 660 Co-K_α (Fe-filtered) intensities measured visually from multiple-film, equi-inclination, Weissenberg photographs.

Refinement of the structure to R 0·13 was accomplished by using a full-matrix least-squares programme,[2] with anisotropic thermal motion for cobalt, chlorine, and nitrogen atoms, on an IBM 360/40 H computer. Attempted refinement based on the alternate space-group Cc gave meaningless positional changes and a minimal decrease in R, thus permitting use of space group $C2/c$. Figure 1 gives the molecular geometry and Figure 2 the [010] projection of the structure.

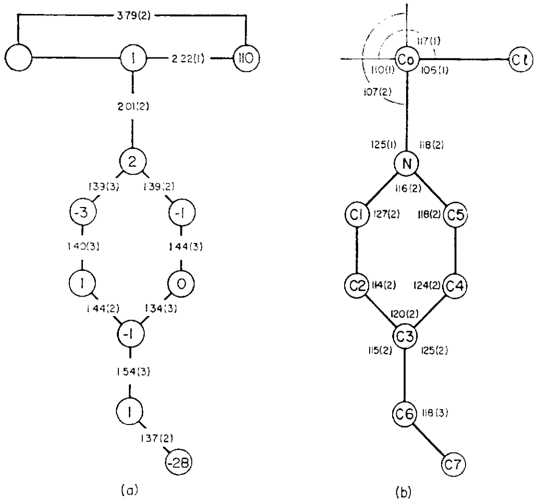

FIGURE 1 *Molecular geometry.* (a) *Bond lengths* (Å) *with standard deviations in parentheses. Deviations from least-squares plane are given in units of* 0·01 Å *in the circles.* (b) *Bond angles in degrees with standard deviations in brackets*

Intermolecular distances are all in accord with known van der Waals radii. Vinyl C—C distances of less than 4 Å were expected according to the topochemical rule of Hirshfeld and Schmidt[3] but were not found. This was unexpected as the crystals polymerize readily at about 100°. Recent work on the isomorphous zinc compound[4] has shown that it is transformed before polymerization at 100° into another structure which does have the expected close approaches between vinyl carbons. Similar behaviour is expected for the cobalt compound, but the phase-change seems to occur at a temperature too close to that of polymerization to allow of its experimental observation.

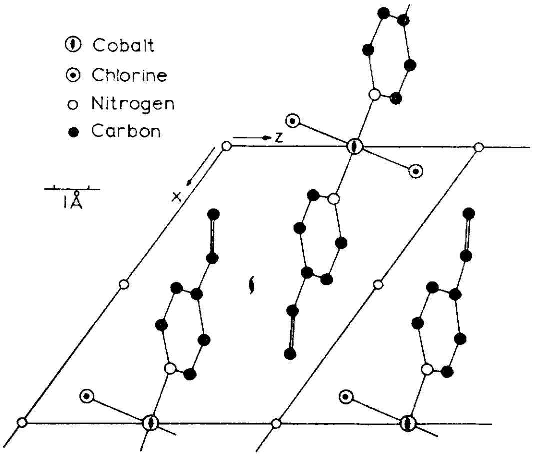

FIGURE 2 *The* [010] *projection of the structure for* a/2 *and* c/2

The crystals decompose slowly on *X*-ray irradiation: this results in low accuracy of intensity measurement and consequently in mediocre accuracy of bond-length and angle determination. The only accurately determined bond length is 2·22 ± 0·01 Å between cobalt and chlorine atoms. This is significantly shorter than that (2·32 ± 0·02 Å) found in the $[CoCl_4]^{2-}$ ion, in the dichrochloride ion, $[CoCl_2H_{11}N_3O]^+$, and in the chlorodinitrotriamininecobalt molecule $CoClH_9N_5O_4$.[5] All other intramolecular distances and angles are similar to tabulated values within experimental errors. The pyridine ring, cobalt, and methylene carbon atoms are found by least-squares methods to be coplanar to 0·03 Å. The N–Co–N and Cl–Co–N angles are close to tetrahedral but the Cl–Co–Cl angle (117 ± 1°) is significantly larger than the tetrahedral value. As the chlorine atoms are 3·79 Å apart, this deviation is not due to overcrowding.

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[1] N. H. Agnew, Ph.D. Thesis, Natal, 1968.

[2] W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A Fortran Crystallographic Least-Squares Program," ORNL-TM-305, 1962.

[3] F. L. Hirshfeld and G. M. L. Schmidt, *J. Polymer Sci., Part A*-1, 1964, **2**, 2181.

[4] C. S. Erasmus and G. Gafner, unpublished.

[5] *Chem. Soc. Special Publ.*, No. 11, 1958.