

## Metal Complexes with Mixed Ligands

### 6. The Molecular and Crystal Structure of Diimidazole Cobalt(II) Dichloride, $\text{Co}(\text{C}_3\text{H}_4\text{N}_2)_2\text{Cl}_2$

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The crystal structure of  $\text{Co}(\text{C}_3\text{H}_4\text{N}_2)_2\text{Cl}_2$  has been determined from three-dimensional X-ray data, collected by the equi-inclination Weissenberg method with the multiple film technique using  $\text{CuK}\alpha$ -radiation. There are four formula units in the monoclinic unit cell, and the cell dimensions are  $a = 7.946 \text{ \AA}$ ,  $b = 11.867 \text{ \AA}$ ,  $c = 12.090 \text{ \AA}$  and  $\beta = 113^\circ 57'$ . The space group is  $P2_1/c$ . The coordination of the cobalt atom is tetrahedral and the bond distances are: Co-N, 1.989 and 1.997  $\text{ \AA}$ ; Co-Cl, 2.264 and 2.237  $\text{ \AA}$ .

It has been found that the zinc ion in native carbonic anhydrase can be removed and a catalytically active Co(II)-enzyme can be made (Lindskog and Malmström, 1962).<sup>1</sup> In human carbonic anhydrase C the zinc ion is surrounded by three histidyl ligands. The fourth ligand of the zinc ion is a water molecule or a hydroxyl ion. The coordination is almost tetrahedral. A distorted tetrahedron surrounding the metal ion in cobalt carbonic anhydrase has been proposed from absorption spectra.<sup>2</sup> In order to study the structural effects caused by a zinc-cobalt exchange, it is of interest to compare imidazole complexes of the two metals. The reason for choosing imidazole is the close relationship of this ligand with biological systems of more complex nature involving histidine residues. The structure of  $\text{Zn}(\text{C}_3\text{H}_4\text{N}_2)_2\text{Cl}_2$  has previously been determined by Lundberg.<sup>3</sup> In this paper we will present the structure of  $\text{Co}(\text{C}_3\text{H}_4\text{N}_2)_2\text{Cl}_2$  and compare it with the structure of the zinc complex.

#### EXPERIMENTAL

*Preparation of the crystals.* The crystals were prepared by separately dissolving 2.72 g (0.04 mol) imidazole in 10 ml of absolute alcohol and 4.76 g (0.02 mol)  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  in 10 ml of absolute alcohol. The two solutions were mixed and deep blue crystals were obtained by slow evaporation of the solution at room temperature.

*Unit cell data.* From rotation photographs (around [001], [010], and [100]) and the corresponding Weissenberg photographs (zero, first, and second layers), taken with  $\text{CuK}\alpha$ -

radiation, it was concluded that the crystals are monoclinic with  $a = 7.95 \text{ \AA}$ ,  $b = 11.82 \text{ \AA}$ ,  $c = 12.02 \text{ \AA}$ , and  $\beta = 113^\circ 59'$ . Data from powder photographs, taken with  $\text{CuK}\alpha$ -radiation in a focusing camera of Guiner-Hägg type, with Si as an internal standard, were refined, and the following result was obtained:  $a = 7.946 \pm 0.001 \text{ \AA}$ ,  $b = 11.867 \pm 0.002 \text{ \AA}$ ,  $c = 12.090 \pm 0.003 \text{ \AA}$ , and  $\beta = 113^\circ 57' \pm 1'$ . By the flotation method, using bromoform and acetone, the density was determined to  $1.68 \text{ g/cm}^3$ . Four formula units  $\text{Co}(\text{C}_3\text{H}_4\text{N}_2)_2\text{Cl}_2$  in the unit cell give a calculated density of  $1.70 \text{ g/cm}^3$ .

*Space group.* The following conditions limiting possible reflexions were found:  $hkl$ : no condition;  $h0l$ :  $l = 2n$ ;  $0k0$ :  $k = 2n$ , which is characteristic for the space group  $P2_1/c$  (No. 14).<sup>4</sup>

*The intensity material.* Equi-inclination Weissenberg films,  $hk0 - hk9$ , were taken with  $\text{CuK}\alpha$ -radiation. The intensities of 1204 independent reflections were estimated visually with the multiple film technique. No absorption correction was made. In order to reduce errors arising from absorption one of the smallest crystals available was used. (The calculated linear absorption coefficient  $\bar{\mu} = 170.4 \text{ cm}^{-1}$ .) The fluorescence from Co did not seriously affect the measurements. The computer programs used were the same as reported in an earlier publication.<sup>5</sup>

#### STRUCTURE DETERMINATION

Since the structure of  $\text{Co}(\text{C}_3\text{H}_4\text{N}_2)_2\text{Cl}_2$  and  $\text{Zn}(\text{C}_3\text{H}_4\text{N}_2)_2\text{Cl}_2$  seemed to be isomorphous, the structure determination of  $\text{Co}(\text{C}_3\text{H}_4\text{N}_2)_2\text{Cl}_2$  was made in the same way as the determination of the  $\text{Zn}(\text{C}_3\text{H}_4\text{N}_2)_2\text{Cl}_2$ -structure.<sup>3</sup> By using the least-squares method the various atomic parameters could be refined to an  $R$ -value equal to 0.124.

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

The above  $R$ -value stands for the isotropic type of refinement and all weights equal to 1 for the reflections where  $0.5 \leq F_o/F_c \leq 2.0$  (91 reflections out of 1204 were thus excluded). For a list of the final atomic parameters, see Table 1. The atomic scattering factors for  $\text{Co}^{2+}$ ,  $\text{Cl}^-$ , N, and C were those given in Int.

Table 1. Atomic positional fractional coordinates and the isotropic thermal parameters with their estimated standard deviations.

	$10^4 \times X$	$10 \times \sigma(X)$	$10^4 \times Y$	$10^4 \times \sigma(Y)$	$10^4 \times Z$	$10^4 \times \sigma(Z)$	$B$	$10^2 \times \sigma(B)$
Co	2430	3	3198	2	2506	2	1.82	6
Cl <sub>1</sub>	2140	5	1404	3	1818	4	2.57	7
Cl <sub>2</sub>	182	5	3638	3	3096	4	2.92	8
N <sub>1</sub>	2530	17	4143	10	1175	13	2.45	22
N <sub>2</sub>	2031	21	251	12	4323	15	3.66	28
N <sub>3</sub>	4836	18	3449	10	3910	13	2.39	22
N <sub>4</sub>	7841	23	3712	13	5003	16	4.03	31
C <sub>1</sub>	1746	27	1074	16	5010	19	3.70	34
C <sub>2</sub>	3359	28	5219	16	1290	20	4.00	36
C <sub>3</sub>	6956	25	595	15	4864	18	3.45	32
C <sub>4</sub>	6474	27	3561	15	3843	19	3.52	32
C <sub>5</sub>	5177	25	1524	14	138	18	3.14	30
C <sub>6</sub>	6940	25	1367	15	759	18	3.35	31

Tables,<sup>6</sup> and accounts were taken of the real part of the dispersion correction for the cobalt and the chlorine atoms. The  $F_{\text{obs}}^i F_{\text{calc}}^i$ -tables are excluded here, but can be obtained on request.

## DESCRIPTION OF THE STRUCTURE

The structure is built up by  $\text{Co}(\text{C}_3\text{H}_4\text{N}_2)_2\text{Cl}_2$  molecules which, as shown below, are held together with hydrogen bonds and van der Waals forces. Interatomic distances and bond angles in the molecule are presented in Table 2.

Table 2. Interatomic distances and bond angles in the molecule and their estimated standard deviations.

	Distance (Å)	$10^3 \times \sigma$		Angles (°)	$\sigma$
Co-N <sub>1</sub>	1.989	14	N <sub>1</sub> -Co-N <sub>3</sub>	105.4	0.5
Co-N <sub>3</sub>	1.997	14	N <sub>1</sub> -Co-Cl <sub>1</sub>	105.3	0.4
N <sub>1</sub> -C <sub>1</sub>	1.314	25	N <sub>1</sub> -Co-Cl <sub>2</sub>	115.2	0.4
C <sub>1</sub> -N <sub>2</sub>	1.359	25	N <sub>3</sub> -Co-Cl <sub>1</sub>	111.8	0.4
N <sub>2</sub> -C <sub>3</sub>	1.407	24	N <sub>3</sub> -Co-Cl <sub>2</sub>	107.9	0.4
C <sub>3</sub> -C <sub>2</sub>	1.387	29	Cl <sub>1</sub> -Co-Cl <sub>2</sub>	111.2	0.2
C <sub>2</sub> -N <sub>1</sub>	1.417	23	N <sub>1</sub> -C <sub>1</sub> -N <sub>2</sub>	113.0	1.6
N <sub>3</sub> -C <sub>4</sub>	1.343	23	C <sub>1</sub> -N <sub>2</sub> -C <sub>3</sub>	106.0	1.6
N <sub>4</sub> -N <sub>4</sub>	1.393	27	N <sub>2</sub> -C <sub>3</sub> -C <sub>2</sub>	106.9	1.6
N <sub>4</sub> -C <sub>5</sub>	1.374	26	C <sub>3</sub> -C <sub>2</sub> -N <sub>1</sub>	107.8	1.7
C <sub>5</sub> -C <sub>5</sub>	1.307	26	C <sub>2</sub> -N <sub>1</sub> -C <sub>1</sub>	106.3	1.5
C <sub>5</sub> -N <sub>3</sub>	1.397	25	N <sub>3</sub> -C <sub>4</sub> -N <sub>4</sub>	109.3	1.7
Co-Cl <sub>1</sub>	2.264	4	C <sub>4</sub> -N <sub>4</sub> -C <sub>5</sub>	104.9	1.6
Co-Cl <sub>2</sub>	2.237	5	N <sub>4</sub> -C <sub>5</sub> -C <sub>5</sub>	110.7	1.8
			C <sub>5</sub> -C <sub>5</sub> -N <sub>3</sub>	108.3	1.6
			C <sub>5</sub> -N <sub>3</sub> -C <sub>4</sub>	106.7	1.5

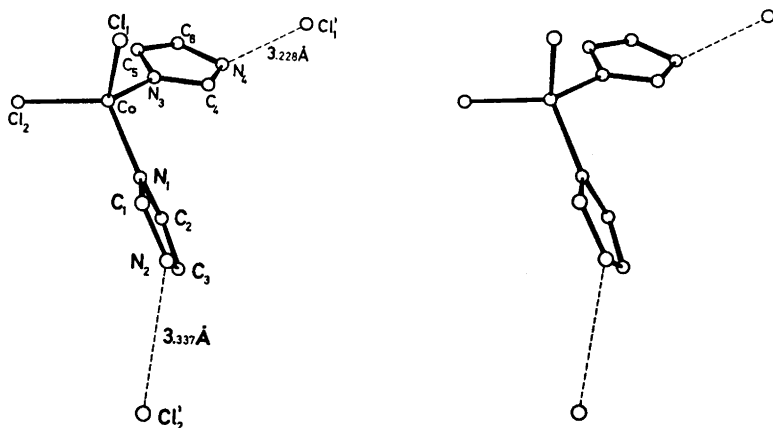


Fig. 1. One formula unit of  $\text{Co}(\text{C}_3\text{H}_4\text{N}_2)_2\text{Cl}_2$  and two hydrogen bonding adjacent chlorine atoms.

The coordination of the cobalt atom is very nearly tetrahedral (Fig. 1). The largest deviation from the tetrahedral angle is  $5.7^\circ$ . The Co-Cl distances are 2.264 and 2.237 Å. The distances from the cobalt atom to the two coordinating nitrogens of the imidazole rings are 1.989 and 1.997 Å. The decrease in the Co-N and the Co-Cl bond lengths compared to those of octahedral coordinated cobalt (2.15–2.20 Å and 2.43–2.63 Å) is of the expected order of magnitude.<sup>7</sup> The bond distances and angles in the imidazole rings lie within the expected range.<sup>3,5,8</sup>

To study the planarity of the imidazole rings, two least-squares planes and the displacement of the nitrogen and carbon atoms from these planes were calculated. The equations for the first plane is:  $-0.8958x + 0.4390y - 0.0694z + 0.7931 = 0$ , and the mean displacement is 0.008 Å. The equation for the second plane is:  $-0.1234x + 0.9900y - 0.0678z + 3.5084 = 0$ , and the mean displacement is 0.009 Å. The distances from the cobalt atom to the two planes are 0.053 Å and  $-0.025$  Å, respectively.

Looking at the pyridine nitrogens in the two imidazole rings and the chlorines situated in neighbouring formula units the following short interatomic distances were found:  $N_2-Cl_2'$  equal to 3.337 Å and  $N_4-Cl_1'$  equal to 3.228 Å. These distances can be compared with the hydrogen bond distances found in  $Zn(C_3H_4N_2)_2Cl_2^3$  which were 3.34 and 3.27 Å. Furthermore they fall well within the range of N-H...Cl distances (3.22–3.59 Å) given by Olovsson (1966).<sup>9</sup> Thus, the separate formula units in the  $Co(C_3H_4N_2)_2Cl_2$ -structure are held together by hydrogen bonds; see Fig. 1. If we assume the hydrogen atoms to lie in the planes of the imidazole rings the angles H-N<sub>2</sub>...Cl<sub>2</sub>' and H-N<sub>4</sub>...Cl<sub>1</sub>' are  $27^\circ 14'$  and  $10^\circ 13'$ , respectively.

Table 3. Intermolecular distances shorter than 4.00 Å.

Distance (Å)	Distance (Å)
Cl <sub>1A</sub> -Cl <sub>2A</sub>	3.71
Cl <sub>1A</sub> -Cl <sub>2E</sub>	3.79
Cl <sub>1A</sub> -N <sub>1A</sub>	3.39
Cl <sub>1A</sub> -N <sub>2C</sub>	3.36
Cl <sub>1A</sub> -N <sub>3A</sub>	3.53
Cl <sub>1A</sub> -N <sub>4F</sub>	3.88
Cl <sub>1A</sub> -C <sub>1A</sub>	3.64
Cl <sub>1A</sub> -C <sub>2F</sub>	3.66
Cl <sub>1A</sub> -C <sub>2F'</sub>	3.74
Cl <sub>1A</sub> -C <sub>5C</sub>	3.74
Cl <sub>1A</sub> -C <sub>6G</sub>	3.80
Cl <sub>2A</sub> -N <sub>1A</sub>	3.57
Cl <sub>2A</sub> -N <sub>3A</sub>	3.43
Cl <sub>2A</sub> -N <sub>4H</sub>	3.50
Cl <sub>2A</sub> -N <sub>4B</sub>	3.84
Cl <sub>2A</sub> -C <sub>1C</sub>	3.72
Cl <sub>2A</sub> -C <sub>3I</sub>	3.81
Cl <sub>2A</sub> -C <sub>4H</sub>	3.42
Cl <sub>2A</sub> -C <sub>5A</sub>	3.73
Cl <sub>2A</sub> -C <sub>6G</sub>	3.99
Cl <sub>2A</sub> -C <sub>6B</sub>	3.88
N <sub>1A</sub> -N <sub>2I</sub>	3.67
N <sub>1A</sub> -C <sub>1I</sub>	3.86
N <sub>1A</sub> -C <sub>4A</sub>	3.54
N <sub>2A</sub> -C <sub>1I</sub>	3.75
N <sub>2A</sub> -C <sub>3K</sub>	3.72
N <sub>3A</sub> -C <sub>2A</sub>	3.58
N <sub>3A</sub> -C <sub>3F</sub>	3.75
N <sub>3A</sub> -C <sub>6B</sub>	3.83
N <sub>3A</sub> -C <sub>6D</sub>	3.82
N <sub>4A</sub> -C <sub>3F</sub>	3.76
C <sub>1A</sub> -C <sub>1I</sub>	3.76
C <sub>1A</sub> -C <sub>2I</sub>	3.84
C <sub>1A</sub> -C <sub>3I</sub>	3.78
C <sub>1A</sub> -C <sub>5C</sub>	3.90
C <sub>2A</sub> -C <sub>4A</sub>	3.65
C <sub>2A</sub> -C <sub>4D</sub>	3.97
C <sub>2A</sub> -C <sub>6B</sub>	3.92
C <sub>3A</sub> -C <sub>3K</sub>	3.55
C <sub>3A</sub> -C <sub>4F</sub>	3.70
C <sub>3A</sub> -C <sub>5F</sub>	3.77
C <sub>3A</sub> -C <sub>6F</sub>	3.77
C <sub>5A</sub> -C <sub>5B</sub>	3.63
C <sub>6A</sub> -C <sub>6B</sub>	3.78

In Table 3 can be seen a list of intermolecular distances shorter than 4.00 Å. These distances are short enough to be classed as van der Waals contacts. Looking at the hydrogen bond system and the possible van der Waals contacts it can be seen that the crystal is essentially built up as a three-dimensional network (see Fig. 2).

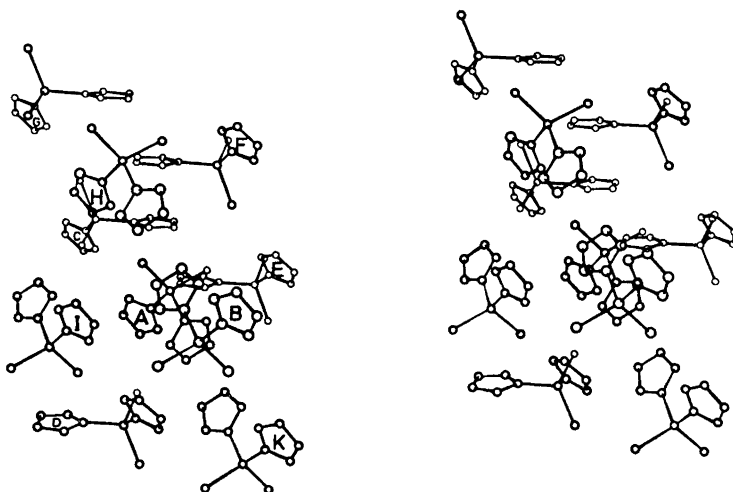


Fig. 2. An illustration of the molecular packing of  $\text{Co}(\text{C}_3\text{H}_4\text{N}_2)_2\text{Cl}_2$ .

#### DISCUSSION

Comparing the structure of  $\text{Zn}(\text{C}_3\text{H}_4\text{N}_2)_2\text{Cl}_2^3$  with the structure of  $\text{Co}(\text{C}_3\text{H}_4\text{N}_2)_2\text{Cl}_2$ , it was found that the two structures are isomorphous. A list showing the cell parameters is presented here:

$\text{Zn}(\text{C}_3\text{H}_4\text{N}_2)_2\text{Cl}_2^3$ :	$\text{Co}(\text{C}_3\text{H}_4\text{N}_2)_2\text{Cl}_2$ :
$a = 7.956 \text{ \AA} \pm 0.005$	$a = 7.946 \text{ \AA} \pm 0.001$
$b = 11.856 \text{ \AA} \pm 0.005$	$b = 11.867 \text{ \AA} \pm 0.002$
$c = 12.078 \text{ \AA} \pm 0.005$	$c = 12.090 \text{ \AA} \pm 0.003$
$\beta = 113^\circ 58' \pm 2'$	$\beta = 113^\circ 57' \pm 1'$
$a : b : c = 1.00 : 1.49 : 1.52$	$a : b : c = 1.00 : 1.49 : 1.52$

The coordination around the metal atoms in both structures is tetrahedral, and the largest difference in the atomic position coordinates is 0.08 Å (the  $x$ -coordinate of the  $\text{C}_6$ -atom). Furthermore, the two structures are similarly built up as a three-dimensional network with the aid of hydrogen bond systems and van der Waals forces. The differences between the two structures are very small and they all fall almost within three times the estimated standard deviations. This suggests that a zinc-cobalt(II) exchange in systems of the presented type will not cause any structural changes of essential importance.

*Acknowledgements.* We thank Professor Nils Ingri for all the facilities placed at our disposal and for his interest in the present work. The English of the present paper has been corrected by Dr. Michael Sharp. This work forms a part of a program supported by *Statens Naturvetenskapliga Forskningsråd*.

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Received May 3, 1972.