

## The Crystal and Molecular Structure of Bis-(1-methyl-3-*o*-chlorophenyltriazene 1-oxide)cobalt(II)

BY G. L. DWIVEDI AND R. C. SRIVASTAVA

*Department of Physics, Indian Institute of Technology, Kanpur-16, India*

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Crystals of bis-(1-methyl-3-*o*-chlorophenyltriazene 1-oxide)cobalt(II) have been subjected to X-ray analysis. They are in the orthorhombic space group  $P2_12_12_1$  with four molecules of  $C_{14}H_{14}N_6O_2Cl_2Co$  in a unit cell of dimensions  $a=19.035$ ,  $b=13.287$  and  $c=7.045$  Å. The heavy atom method was used. Refinement was carried out by the full-matrix least-squares method using 853 observed reflexions. The final  $R$  index is 0.077. Two ligands in the complex are in *cis* positions to each other and function as tridentate with O,N and Cl as coordinating atoms. The chlorine atoms which are also attached to the benzene rings were found to be very weakly coordinated to the cobalt ion completing a distorted octahedral coordination. The Co-Cl distance is 2.98 Å. All other bond distances and angles are normal.

### Introduction

Bis-(1-methyl-3-*o*-chlorophenyltriazene 1-oxide) cobalt (II) has been prepared by the reaction of triazene-1-oxide with cobalt acetate in methanolic medium by Zacharias & Chakravorty (1969). They suspected that on the basis of magnetic moment and electronic spectral measurements the chlorine atom attached to the phenyl group was coordinated with the metal. This chlorine coordination is a very unusual structural feature and has not been observed in any similar complex (Chakravorty, Behera & Zacharias, 1968; Behera & Chakravorty, 1969). The present investigation provides conclusive evidence for the above mentioned novel structural feature.

### Experimental

Crystallization from methanol at room temperature yielded crystals of the cobalt complex which were red in colour and elongated along the  $c$  axis. Faces {110} were well developed. Copper  $K\alpha$  radiation ( $\lambda=1.542$  Å) was employed for X-ray measurements. Preliminary studies were made with a Weissenberg camera. Rotation, oscillation and Weissenberg photographs were taken about [001] and [010]. From the systematic absences the space group was uniquely determined as  $P2_12_12_1$ . Accurate cell dimensions were later determined on a General Electric diffractometer. The crystal data are listed in Table 1.

Density was measured by flotation in an aqueous solution of  $ZnCl_2$ . The average of several such measurements is given in Table 1.

Intensities were measured on a General Electric diffractometer equipped with a quarter-circle single crystal orienter. A crystal with dimensions approximately  $0.3 \times 0.2 \times 0.5$  mm was mounted parallel to [001].  $\varphi$ ,  $\chi$  and  $2\theta$  settings for all reflexions in the Cu-sphere were calculated using accurately determined cell parameters. The intensity data were collected with the stationary-crystal stationary-counter technique using filtered Cu

$K\alpha$  radiation. Reflexions which differed from the background count by more than one standard deviation were considered observed and the rest unobserved. The data were not collected beyond  $2\theta=120^\circ$ , because it was found that at this setting 66% of the reflexions were unobserved. A total of 1043 reflexions were measured, of which 853 gave measurable intensity.

Table 1. *Crystal data of  
bis-(1-methyl-3-*o*-chlorophenyltriazene  
1-oxide)cobalt(II)*

|                            |   |
|----------------------------|---|
| $C_{14}H_{14}N_6O_2Cl_2Co$ |   |
| $a=19.035 \pm 0.005$ Å     | Melting point $153^\circ C$                                       |
| $b=13.287 \pm 0.006$       | M.W. 428.14   |
| $c=7.045 \pm 0.004$        | $V=1781.78$ Å <sup>3</sup>  |
| Systematic absences        |   |
| $h00$ $h=2n+1$             | $D_m=1.52$ g.cm <sup>-3</sup>                                     |
| $0k0$ $k=2n+1$             | $D_c=1.59$ g.cm <sup>-3</sup>                                     |
| $00l$ $l=2n+1$             | $\mu=103.4$ cm <sup>-1</sup> . (Cu $K\alpha$ , $\lambda=1.542$ Å) |
| Space group                |   |
| $P2_12_12_1$ (No. 19)      |   |

During intensity measurement, six reflexions 040, 800, 330, 730, 752 and 004 were monitored at intervals of six hours to check any damage due to irradiation of the crystal, exposure to atmosphere or any other effect. No appreciable variations in intensity were observed.

The variation of intensity as a function of  $\varphi$  was plotted for 001 reflexions aligned at  $\chi=90^\circ$ . An empirical absorption correction (Furnas, 1956) as a function of  $\varphi$  and  $2\theta$  was determined on the basis of these plots and applied to all reflexions. Owing to the small and fairly regular size of the crystals such corrections were small, the maximum being 1.2.

### Solution and refinement of the structure

Unobserved reflexions were given half the intensity of the weakest observed reflexion and then the data were corrected for Lorentz and polarization factors.



Table 2 (cont.)

| H 10 2 |      |      | H 5 3 |      |      | H 4 4 |      |      | H 9 4 |      |      | H 7 5 |      |      |
|--------|------|------|-------|------|------|-------|------|------|-------|------|------|-------|------|------|
| 0      | 21.7 | 6.5  | 0     | 6.8* | 7.2  | 0     | 53.5 | 5.6  | 0     | 11.6 | 16.2 | 0     | 13.0 | 13.3 |
| 1      | 20.8 | 19.5 | 1     | 21.8 | 20.8 | 1     | 68.8 | 7.1  | 1     | 11.6 | 25.7 | 1     | 13.0 | 9.5  |
| 2      | 20.6 | 21.5 | 2     | 24.3 | 24.6 | 2     | 50.5 | 5.9  | 2     | 10.1 | 25.7 | 2     | 8.9* | 4.1  |
| 3      | 8.5* | 18.1 | 3     | 6.7* | 4.4  | 3     | 37.6 | 3.8  | 3     | 10.1 | 11.1 | 3     | 23.1 | 18.6 |
| 4      | 16.0 | 17.6 | 4     | 30.2 | 29.9 | 4     | 27.7 | 24.2 | 4     | 7.0* | 2.3  | 4     | 16.8 | 12.4 |
| 5      | 8.5* | 5.6  | 5     | 30.8 | 34.5 | 5     | 14.9 | 1.5  | 5     | 17.4 | 13.8 | 5     | 21.4 | 23.8 |
| 6      | 19.4 | 20.3 | 6     | 33.8 | 23.6 | 6     | 14.3 | 14.7 | 6     | 12.5 | 9.3  | 6     | 21.8 | 22.3 |
| 7      | 8.6* | 5.6  | 7     | 33.1 | 23.2 | 7     | 14.5 | 15.2 | 7     | 8.6* | 6.7  | 7     | 8.4  | 13.0 |
| 8      | 24.0 | 18.9 | 8     | 33.7 | 36.6 | 8     | 70.3 | 35.3 | 8     | 8.6* | 12.6 | 8     | 20.1 | 15.9 |
| 9      | 8.5* | 6.5  | 9     | 28.4 | 25.9 | 9     | 16.0 | 31.7 | 9     | 10.0 | 2.1  | 9     | 8    | 0    |
| 10     | 8.2* | 7.8  | 10    | 38.4 | 41.5 | 10    | 38.4 | 31.1 | 10    | 10.4 | 17.3 | 10    | 8    | 0    |
| 11     | 8.2* | 2.9  | 11    | 7.6* | 6.0  | 11    | 27.2 | 26.4 | 11    | 7.7* | 7.1  | 11    | 15.0 | 12.2 |
| 0      | 8.9  | 0.1  | 12    | 13.7 | 14.9 | 12    | 21.8 | 26.4 | 12    | 7.8* | 2.9  | 12    | 13.2 | 13.9 |
| 1      | 10.9 | 11.7 | 13    | 28.5 | 25.7 | 13    | 19.5 | 16.4 | 13    | 12.0 | 19.6 | 13    | 10.1 | 8.1  |
| 2      | 16.9 | 19.3 | 14    | 11.5 | 5.4  | 14    | 24.9 | 22.3 | 14    | 13.0 | 18.7 | 14    | 5.8  | 8.4  |
| 3      | 17.1 | 18.1 | 15    | 7.7* | 5.4  | 15    | 11.2 | 11.8 | 15    | 12.0 | 6.9  | 15    | 12.9 | 10.1 |
| 4      | 4.3  | 6.8  |       |      |      |       |      |      |       |      |      |       |      |      |
| 5      | 13.4 | 14.0 |       |      |      |       |      |      |       |      |      |       |      |      |
| 6      | 8.6* | 7.0  |       |      |      |       |      |      |       |      |      |       |      |      |
| 7      | 13.0 | 15.6 |       |      |      |       |      |      |       |      |      |       |      |      |
| 8      | 13.2 | 12.3 |       |      |      |       |      |      |       |      |      |       |      |      |
| 9      | 12   | 2    |       |      |      |       |      |      |       |      |      |       |      |      |
| 0      | 8.9* | 2.4  |       |      |      |       |      |      |       |      |      |       |      |      |
| 1      | 17.9 | 19.1 |       |      |      |       |      |      |       |      |      |       |      |      |
| 2      | 8.6* | 4.8  |       |      |      |       |      |      |       |      |      |       |      |      |
| 3      | 8.7* | 4.4  |       |      |      |       |      |      |       |      |      |       |      |      |
| 4      | 15.8 | 13.2 |       |      |      |       |      |      |       |      |      |       |      |      |
| 5      | 4.7  | 15.6 |       |      |      |       |      |      |       |      |      |       |      |      |
| 6      | 8.9  | 9    |       |      |      |       |      |      |       |      |      |       |      |      |
| 7      | 44.6 | 48.8 |       |      |      |       |      |      |       |      |      |       |      |      |
| 8      | 16.2 | 21.3 |       |      |      |       |      |      |       |      |      |       |      |      |
| 9      | 5.3  | 19.1 |       |      |      |       |      |      |       |      |      |       |      |      |
| 10     | 6.9  | 48.8 |       |      |      |       |      |      |       |      |      |       |      |      |
| 11     | 7.2* | 2.7  |       |      |      |       |      |      |       |      |      |       |      |      |
| 12     | 34.1 | 32.7 |       |      |      |       |      |      |       |      |      |       |      |      |
| 13     | 7.5* | 7.3  |       |      |      |       |      |      |       |      |      |       |      |      |
| 14     | 12.0 | 11.1 |       |      |      |       |      |      |       |      |      |       |      |      |
| 15     | 7.7* | 11.9 |       |      |      |       |      |      |       |      |      |       |      |      |
| 16     | 7.6* | 5.2  |       |      |      |       |      |      |       |      |      |       |      |      |
| 0      | 7.4  | 7.6  |       |      |      |       |      |      |       |      |      |       |      |      |
| 1      | 18.6 | 18.2 |       |      |      |       |      |      |       |      |      |       |      |      |
| 2      | 38.4 | 43.2 |       |      |      |       |      |      |       |      |      |       |      |      |
| 3      | 61.6 | 30.9 |       |      |      |       |      |      |       |      |      |       |      |      |
| 4      | 15.7 | 20.6 |       |      |      |       |      |      |       |      |      |       |      |      |
| 5      | 62.0 | 65.4 |       |      |      |       |      |      |       |      |      |       |      |      |
| 6      | 28.5 | 28.0 |       |      |      |       |      |      |       |      |      |       |      |      |
| 7      | 14.4 | 13.4 |       |      |      |       |      |      |       |      |      |       |      |      |
| 8      | 6.1* | 8.3  |       |      |      |       |      |      |       |      |      |       |      |      |
| 9      | 31.2 | 38.6 |       |      |      |       |      |      |       |      |      |       |      |      |
| 10     | 13.1 | 17.4 |       |      |      |       |      |      |       |      |      |       |      |      |
| 11     | 60.3 | 62.5 |       |      |      |       |      |      |       |      |      |       |      |      |
| 12     | 18.9 | 21.3 |       |      |      |       |      |      |       |      |      |       |      |      |
| 13     | 39.7 | 36.0 |       |      |      |       |      |      |       |      |      |       |      |      |
| 14     | 22.7 | 23.2 |       |      |      |       |      |      |       |      |      |       |      |      |
| 15     | 7.7* | 7.4  |       |      |      |       |      |      |       |      |      |       |      |      |
| 16     | 7.7* | 8.0  |       |      |      |       |      |      |       |      |      |       |      |      |
| 0      | 5.5  | 5.3  |       |      |      |       |      |      |       |      |      |       |      |      |
| 1      | 24.0 | 27.5 |       |      |      |       |      |      |       |      |      |       |      |      |
| 2      | 50.6 | 55.1 |       |      |      |       |      |      |       |      |      |       |      |      |
| 3      | 39.3 | 42.2 |       |      |      |       |      |      |       |      |      |       |      |      |
| 4      | 32.5 | 33.6 |       |      |      |       |      |      |       |      |      |       |      |      |
| 5      | 18.2 | 14.4 |       |      |      |       |      |      |       |      |      |       |      |      |
| 6      | 5.8* | 8.1  |       |      |      |       |      |      |       |      |      |       |      |      |
| 7      | 6.0* | 4.1  |       |      |      |       |      |      |       |      |      |       |      |      |
| 8      | 27.9 | 26.9 |       |      |      |       |      |      |       |      |      |       |      |      |
| 9      | 15.4 | 20.3 |       |      |      |       |      |      |       |      |      |       |      |      |
| 10     | 44.8 | 46.0 |       |      |      |       |      |      |       |      |      |       |      |      |
| 11     | 31.4 | 32.1 |       |      |      |       |      |      |       |      |      |       |      |      |
| 12     | 45.7 | 39.5 |       |      |      |       |      |      |       |      |      |       |      |      |
| 13     | 28.8 | 26.7 |       |      |      |       |      |      |       |      |      |       |      |      |
| 14     | 13.5 | 18.6 |       |      |      |       |      |      |       |      |      |       |      |      |
| 15     | 11.4 | 11.6 |       |      |      |       |      |      |       |      |      |       |      |      |
| 16     | 7.7* | 7.3  |       |      |      |       |      |      |       |      |      |       |      |      |
| 0      | 25.3 | 21.3 |       |      |      |       |      |      |       |      |      |       |      |      |
| 1      | 30.6 | 24.0 |       |      |      |       |      |      |       |      |      |       |      |      |
| 2      | 34.7 | 33.1 |       |      |      |       |      |      |       |      |      |       |      |      |
| 3      | 52.8 | 49.0 |       |      |      |       |      |      |       |      |      |       |      |      |
| 4      | 45.6 | 48.1 |       |      |      |       |      |      |       |      |      |       |      |      |
| 5      | 46.0 | 37.8 |       |      |      |       |      |      |       |      |      |       |      |      |
| 6      | 29.9 | 37.8 |       |      |      |       |      |      |       |      |      |       |      |      |
| 7      | 12.6 | 14.2 |       |      |      |       |      |      |       |      |      |       |      |      |
| 8      | 39.6 | 42.0 |       |      |      |       |      |      |       |      |      |       |      |      |
| 9      | 24.3 | 30.1 |       |      |      |       |      |      |       |      |      |       |      |      |
| 10     | 38.4 | 40.1 |       |      |      |       |      |      |       |      |      |       |      |      |
| 11     | 10.9 | 12.6 |       |      |      |       |      |      |       |      |      |       |      |      |
| 12     | 18.1 | 10.5 |       |      |      |       |      |      |       |      |      |       |      |      |
| 13     | 27.0 | 25.9 |       |      |      |       |      |      |       |      |      |       |      |      |
| 14     | 11.8 | 7.4  |       |      |      |       |      |      |       |      |      |       |      |      |
| 15     | 7.6* | 7.9  |       |      |      |       |      |      |       |      |      |       |      |      |
| 0      | 47.1 | 48.5 |       |      |      |       |      |      |       |      |      |       |      |      |
| 1      | 25.2 | 24.6 |       |      |      |       |      |      |       |      |      |       |      |      |
| 2      | 46.5 | 46.7 |       |      |      |       |      |      |       |      |      |       |      |      |
| 3      | 36.4 | 29.2 |       |      |      |       |      |      |       |      |      |       |      |      |
| 4      | 19.2 | 24.7 |       |      |      |       |      |      |       |      |      |       |      |      |
| 5      | 20.5 | 19.9 |       |      |      |       |      |      |       |      |      |       |      |      |
| 6      | 37.5 | 34.3 |       |      |      |       |      |      |       |      |      |       |      |      |
| 7      | 5.8  | 8.1  |       |      |      |       |      |      |       |      |      |       |      |      |
| 8      | 45.3 | 43.9 |       |      |      |       |      |      |       |      |      |       |      |      |
| 9      | 25.2 | 28.7 |       |      |      |       |      |      |       |      |      |       |      |      |
| 10     | 41.2 | 39.3 |       |      |      |       |      |      |       |      |      |       |      |      |
| 11     | 15.6 | 18.6 |       |      |      |       |      |      |       |      |      |       |      |      |
| 12     | 25.0 | 23.9 |       |      |      |       |      |      |       |      |      |       |      |      |
| 13     | 14.0 | 13.6 |       |      |      |       |      |      |       |      |      |       |      |      |
| 14     | 12.5 | 12.2 |       |      |      |       |      |      |       |      |      |       |      |      |
| 15     | 7.7* | 8.5  |       |      |      |       |      |      |       |      |      |       |      |      |
| 16     | 16.0 | 20.2 |       |      |      |       |      |      |       |      |      |       |      |      |

synthesis was calculated with phase angles appropriate to the cobalt atom alone and from this both the chlorine atoms and N(6) were located. These atoms were included in the calculation of a second set of structure amplitudes and phase angles. An overall isotropic temperature fac-

tor  $B$  of  $3 \text{ \AA}^2$  was assumed. At this stage the reliability index  $R$  (defined as  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ) was 0.42.

A second three-dimensional Fourier synthesis revealed the positions of N(2), N(3), N(4), N(5), O(1), O(2), C(13), and C(7). After inclusion of these atoms the value

Table 3. The final atomic parameters in the structure of bis-(1-methyl-3-o-chlorophenyltriazeno 1-oxide)cobalt (II)

Numbers in parentheses are standard deviations. Anisotropic temperature factors are of the form:

$$\exp [-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)].$$

All values have been multiplied by  $10^4$ .

|       | x          | y         | z          | $b_{11}$ | $b_{22}$ | $b_{33}$ | $b_{12}$ | $b_{13}$ | $b_{23}$ |
|-------|------------|-----------|------------|----------|----------|----------|----------|----------|----------|
| Co    | 356 (2)    | 1832 (3)  | 849 (5)    | 19 (0)   | 57 (2)   | 216 (7)  | -6 (1)   | -5 (3)   | 6 (4)    |
| Cl(1) | 937 (3)    | 363 (4)   | -1854 (9)  | 26 (2)   | 58 (4)   | 283 (16) | -7 (2)   | -12 (5)  | -56 (7)  |
| Cl(2) | 374 (3)    | -42 (4)   | 3263 (9)   | 16 (1)   | 76 (4)   | 329 (17) | 4 (2)    | -4 (5)   | 64 (8)   |
| O(1)  | 490 (6)    | 2573 (10) | 3290 (18)  | 14 (4)   | 72 (10)  | 210 (35) | 1 (6)    | 6 (11)   | 9 (18)   |
| O(2)  | -52 (6)    | 2474 (9)  | -1444 (17) | 30 (5)   | 39 (8)   | 153 (39) | -10 (6)  | 1 (11)   | -7 (18)  |
| N(1)  | 1159 (8)   | 2594 (13) | 3781 (26)  | 26 (6)   | 54 (13)  | 258 (56) | 9 (8)    | 48 (16)  | -20 (24) |
| N(2)  | 1620 (9)   | 2294 (12) | 2754 (24)  | 40 (7)   | 40 (12)  | 156 (48) | -17 (8)  | -38 (16) | -7 (20)  |
| N(3)  | 1409 (7)   | 1861 (12) | 1065 (25)  | 19 (5)   | 38 (11)  | 263 (51) | 2 (7)    | -1 (15)  | 80 (24)  |
| N(4)  | -654 (7)   | 2002 (10) | -1979 (23) | 20 (5)   | 28 (10)  | 217 (44) | 3 (6)    | 11 (14)  | 10 (21)  |
| N(5)  | -938 (8)   | 1318 (11) | -827 (22)  | 21 (5)   | 61 (12)  | 126 (40) | 0 (7)    | -3 (16)  | -20 (21) |
| N(6)  | -571 (7)   | 1127 (11) | 781 (26)   | 11 (5)   | 35 (10)  | 281 (50) | 4 (6)    | -20 (14) | 18 (23)  |
| C(1)  | 1912 (9)   | 1568 (13) | -253 (27)  | 19 (7)   | 38 (14)  | 161 (59) | 1 (8)    | -4 (17)  | 21 (24)  |
| C(2)  | 2628 (10)  | 1973 (14) | -111 (34)  | 22 (8)   | 41 (13)  | 361 (77) | 2 (8)    | 29 (20)  | 44 (31)  |
| C(3)  | 3122 (11)  | 1691 (16) | -1468 (37) | 31 (8)   | 37 (15)  | 415 (90) | 1 (9)    | 18 (23)  | -51 (32) |
| C(4)  | 2946 (11)  | 1063 (17) | -2977 (40) | 23 (7)   | 75 (17)  | 457 (87) | 3 (10)   | 40 (24)  | -24 (39) |
| C(5)  | 2276 (12)  | 614 (16)  | -3194 (37) | 41 (9)   | 60 (15)  | 296 (73) | 15 (10)  | 28 (24)  | 65 (32)  |
| C(6)  | 1795 (9)   | 878 (14)  | -1747 (31) | 20 (7)   | 37 (13)  | 188 (59) | -12 (8)  | -20 (19) | -46 (26) |
| C(7)  | 1337 (12)  | 3093 (16) | 5529 (31)  | 51 (9)   | 53 (15)  | 177 (60) | -1 (11)  | -14 (20) | -47 (28) |
| C(8)  | -919 (10)  | 535 (11)  | 2058 (28)  | 30 (6)   | 11 (8)   | 193 (50) | -9 (7)   | 20 (18)  | 2 (20)   |
| C(9)  | -1669 (10) | 549 (15)  | 2228 (33)  | 20 (6)   | 47 (15)  | 319 (73) | -5 (9)   | -0 (19)  | 32 (33)  |
| C(10) | -1985 (10) | -56 (16)  | 3553 (35)  | 33 (8)   | 49 (15)  | 360 (81) | -16 (10) | -19 (22) | 53 (33)  |
| C(11) | -1611 (10) | -566 (15) | 4961 (35)  | 18 (7)   | 57 (15)  | 399 (82) | 3 (8)    | 23 (19)  | 78 (32)  |
| C(12) | -871 (11)  | -556 (13) | 4888 (29)  | 35 (9)   | 22 (12)  | 222 (63) | -4 (9)   | 10 (20)  | -7 (25)  |
| C(13) | -547 (8)   | -14 (13)  | 3368 (27)  | 13 (6)   | 48 (12)  | 199 (56) | -6 (7)   | -7 (16)  | -15 (26) |
| C(14) | -979 (11)  | 2283 (16) | -3717 (28) | 41 (7)   | 79 (15)  | 146 (49) | 10 (9)   | -31 (17) | 15 (22)  |

of  $R$  decreased to 0.32. The third three-dimensional Fourier synthesis revealed all the atoms except C(9) and C(14). One cycle of full-matrix least-squares refinement of the atomic coordinates was performed using the program *ORFLS* of Busing, Martin & Levy (1962). The fourth three-dimensional Fourier synthesis revealed all 25 non-hydrogen atoms. The  $R$  value decreased to 0.173.

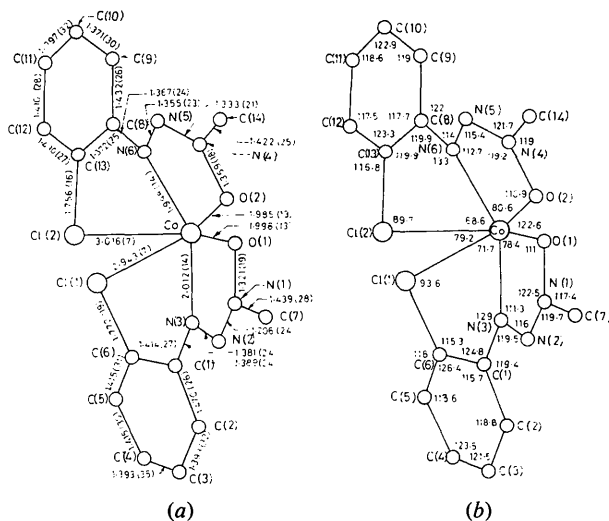


Fig. 1. (a) Bond lengths in Å. Numbers in brackets give standard deviation  $\times 10^3$  Å. (b) Angles in  $^\circ$  in bis-(1-methyl-3-o-chlorophenyltriazeno 1-oxide)cobalt(II).

Table 4. Calculated atomic coordinates for hydrogen atoms

All values have been multiplied by  $10^4$ . All hydrogen atoms were assigned the isotropic temperature factor,  $B=5.0$  Å $^2$ .

|       | x     | y     | z     |
|-------|-------|-------|-------|
| H(1)  | 2770  | 2300  | 1116  |
| H(2)  | 3582  | 2027  | -1434 |
| H(3)  | 3335  | 0864  | -3800 |
| H(4)  | 2120  | 0323  | -4497 |
| H(5)  | 1420  | 3850  | 5280  |
| H(6)  | 1810  | 2890  | 5950  |
| H(7)  | 0980  | 2980  | 6490  |
| H(8)  | -1961 | 0690  | 0929  |
| H(9)  | -2499 | 0013  | 3877  |
| H(10) | -1872 | -1142 | 5672  |
| H(11) | -0586 | -0929 | 5866  |
| H(12) | -1300 | 2860  | -3500 |
| H(13) | -1280 | 1730  | -4200 |
| H(14) | -0613 | 2468  | -4672 |

Two cycles of least-squares refinement were carried out with isotropic temperature factors for each atom which decreased the  $R$  value to 0.14; this was followed by one cycle of least-squares refinement on positional parameters which reduced  $R$  to 0.13. The absorption correction described above and also the dispersion corrections for Co were applied at this stage. To account for dispersion, an effective atomic scattering factor  $f$  for the cobalt ion was taken to be  $f = \sqrt{[(f_0 - A')^2 + A''^2]}$  where  $f_0$  is the atomic scattering factor usually tabulated and  $A'$  and  $A''$  are real and imaginary dispersion corrections (Zachariasen & Ellinger, 1963). This reduced the  $R$  value to 0.115. At this stage anisotropic temper-

ature factors were introduced for all the atoms and two cycles of refinement on temperature factors reduced the  $R$  value to 0.092.

Three more cycles of refinement for positional and anisotropic temperature factors were performed which improved the  $R$  value to 0.082. The least-squares refinement was stopped at this stage because shifts in each parameter were less than half of its standard deviation. The quantity minimized in the least-squares calculation was  $\sum W||F_o| - |F_c||$ , with  $W=1$  for all reflexions. Positional and thermal parameters with their standard deviations are listed in Table 3.

A difference synthesis was then calculated. At a few places, indications of small peaks were found which could be assigned to hydrogen atoms, but these indications were few and in general, very weak. In the case of both methyl groups, one peak in the difference map could be easily identified as a hydrogen atom [H(5) and H(13)]. This fixed one C-H bond in each methyl group. The rest of the hydrogen atoms of a methyl group were calculated on the basis of tetrahedral geometry. The positions of the hydrogen atoms attached to the benzene ring were calculated on the basis of

trigonal geometry in the plane and are listed in Table 4. For all the hydrogen atoms, the C-H distances were assumed to be 1 Å; the temperature factors were assumed to be isotropic and were given the value  $5 \text{ \AA}^2$ . Struc-

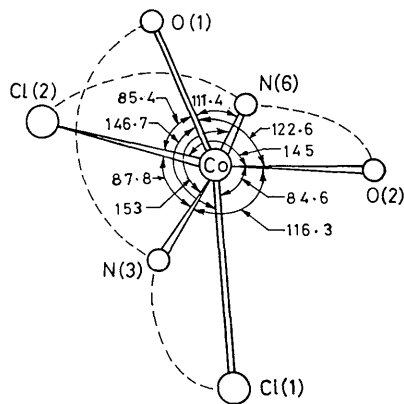


Fig. 2. Distorted octahedral coordination of  $Co^{2+}$  ion. Atoms connected with one set of broken lines belong to the same ligand.

Table 5. Average bond lengths

| Complex   | 1<br>Co-Cl | 2<br>C-Cl | 3<br>C-C<br>phenyl | 4<br>N-C<br>phenyl | 5<br>Co-N | 6<br>N-N | 7<br>N-CH <sub>3</sub> | 8<br>O-N       | 9<br>Co-O      |
|---|------------|-----------|--------------------|--------------------|-----------|----------|------------------------|----------------|----------------|
| Bis-(1-methyl-3- <i>o</i> -chlorophenyltriazene 1-oxide)cobalt(II).   | 2.98 Å     | 1.76 Å    | 1.41 Å             | 1.38 Å             | 2.00 Å    | 1.32 Å   | 1.43 Å                 | 1.34 Å         | 1.99 Å         |
| Bis-(5-chlorosalicylaldoximate)Cu(II) (Orioli, Lingafelter & Brown, 1964).                                  | —          | 1.76      | 1.40               | —                  | —         | —        | —                      | —              | —              |
| Bis(salicylaldehyde)ethylene diiminecobalt(II) monochloroformate (Schaefer & Marsh, 1969).                  | —          | 1.74      | 1.39               | 1.28               | 1.85      | —        | 1.48                   | —              | 1.85           |
| <i>N,N'</i> -Ethylenebis(salicylaldehydeimine)cobalt(II) (Bruckner, Calligaris, Nardin & Randaccio, 1969).  | —          | —         | 1.40               | 1.33               | 1.88      | —        | 1.45                   | —              | 1.92           |
| Diazoaminobenzene Cu(I) (Brown & Dunitz, 1961).   | —          | —         | 1.40               | 1.44               | —         | 1.30     | —                      | —              | —              |
| Cobalt(III) derivative of 1,3-diphenyltriazene(1) (Corbett & Hoskins, 1967).                                | —          | —         | —                  | —                  | 1.93      | 1.31     | —                      | —              | —              |
| Carbonatotetra-amine-cobalt(III) ion (Barclay & Hoskins, 1962).   | —          | —         | —                  | —                  | 1.97      | —        | —                      | —              | 1.90           |
| Interatomic distances in metal chelates of acetylacetonel salicylaldehydeimine (Lingafelter & Braun, 1966). | —          | —         | 1.39               | —                  | 1.94      | —        | —                      | —              | { 1.86<br>1.96 |
| Nickel salicylaldoxime (Merritt, Guare & Lessor, 1956).   | —          | —         | —                  | —                  | —         | —        | —                      | 1.35           | —              |
| Nickel dimethylglyoxime (Godycki & Rundle, 1953).   | —          | —         | —                  | —                  | —         | —        | —                      | { 1.37<br>1.38 | —              |

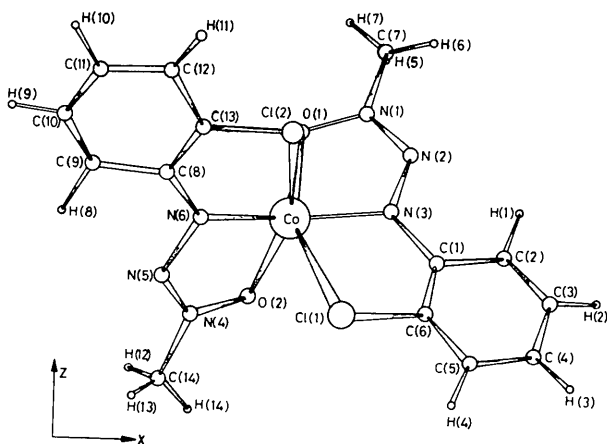
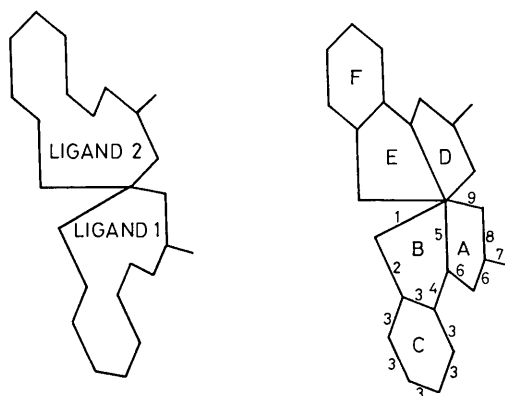


Fig. 3. Projection of the molecule on (010).

Fig. 4. Outline of the present complex as it appears projected down the *c* axis. *A, B, C* and *D, E, F* are the parts of ligands each of which is a plane. The numbers identify the different bonds as given in Table 5.

ture factor calculations including these atoms gave the final *R* value of 0.077.

Atomic form factors for  $\text{Co}^{2+}$ , Cl, N, O, C, H and real and imaginary parts of dispersion corrections were taken from *International Tables for X-ray Crystallography* (1968).

### Discussion of the structure

#### (i) Coordination polyhedra; chlorine coordination

The cobalt atom is surrounded by six atoms, one Cl, one N and one O belonging to one ligand molecule and three equivalent atoms belonging to the other. The chlorine atoms of the two ligand molecules are in *cis* positions as shown in Fig. 1. The average Co–O and Co–N distances are 1.992 and 2.005 Å respectively which may be compared with those observed in other similar compounds (Table 5). The Co–Cl distance is found to be 2.98 Å which is significantly longer than Co–Cl distances (2.23 to 2.49 Å) in similar compounds; cobalt dipyrindine dichloride (Dunitz, 1957),  $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$  (Morosin & Graeber, 1963),  $\text{Co}(\text{AlCl}_4)_2$  (Ibers, 1962),  $\text{Cs}_3\text{CoCl}_5$  (Figgis, Gerloch & Mason, 1964),  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (Mizuno, 1960) and dichloro(ethylenedimorpholine)-cobalt(II) (Scheidt, Hanson & Rasmussen, 1969) *etc.*

The Co–Cl distance of 2.98 Å is certainly too long to be regarded as a coordination bond. However, the chlorine atoms are properly located to form a distorted octahedron around the cobalt ion with the two oxygen and nitrogen atoms. This fact, combined with the results obtained by magnetic and spectroscopic measurements mentioned earlier, strongly suggests that the ligand functions as a tridentate with O, N and Cl as coordinating atoms. The unusually long Cc–Cl distance represents very weak bonding.

The coordination octahedron is severely distorted as

Table 6. Selected bond angles ( $^\circ$ ) in bis-(1-methyl-3-*o*-chlorophenyltriazeno 1-oxide)cobalt(II)

Standard deviations are given in parentheses.

|                   |             |                   |             |
|-------------------|-------------|-------------------|-------------|
| Cl(1)–Co—Cl(2)    | 79.2 (0.2)  | C(10)–C(11)–C(12) | 118.6 (2.0) |
| Cl(1)–Co—N(3)     | 71.7 (0.5)  | C(11)–C(12)–C(13) | 117.5 (1.8) |
| N(3)–Co—O(1)      | 78.4 (0.6)  | C(12)–C(13)–C(8)  | 123.3 (1.5) |
| O(1)–Co—O(2)      | 122.6 (0.5) | Co—Cl(1)–C(6)     | 93.6 (0.7)  |
| O(2)–Co—N(6)      | 80.6 (0.6)  | Cl(1)–C(6)–C(1)   | 115.3 (1.4) |
| N(6)–Co—Cl(2)     | 68.6 (0.5)  | Cl(1)–C(6)–C(5)   | 118.1 (1.6) |
| Co—Cl(2)–C(13)    | 89.7 (0.6)  | C(6)–C(1)–N(3)    | 124.8 (1.6) |
| Cl(2)–C(13)–C(8)  | 119.9 (1.4) | C(1)–N(3)–Co      | 129.0 (1.3) |
| Cl(2)–C(13)–C(12) | 116.8 (1.4) | C(2)–C(1)–N(3)    | 119.4 (1.7) |
| C(13)–C(8)–N(6)   | 119.9 (1.6) | C(1)–N(3)–N(2)    | 119.5 (1.5) |
| C(8)–N(6)–Co      | 133.0 (1.4) | Co—N(3)–N(2)      | 111.3 (1.2) |
| C(9)–C(8)–N(6)    | 122.0 (1.7) | N(3)–N(2)–N(1)    | 116.3 (1.7) |
| C(8)–N(6)–N(5)    | 114.1 (1.4) | N(2)–N(1)–O(1)    | 122.5 (1.7) |
| Co—N(6)–N(5)      | 112.7 (1.2) | N(2)–N(1)–C(7)    | 119.7 (1.7) |
| N(6)–N(5)–N(4)    | 115.3 (1.4) | C(7)–N(1)–O(1)    | 117.4 (1.6) |
| N(5)–N(4)–C(14)   | 121.7 (1.5) | N(1)–O(1)–Co      | 111.0 (1.1) |
| C(14)–N(4)–O(2)   | 119.0 (1.5) | C(6)–C(1)–C(2)    | 115.7 (1.7) |
| N(5)–N(4)–O(2)    | 119.2 (1.5) | C(1)–C(2)–C(3)    | 118.8 (1.9) |
| N(4)–O(2)–Co      | 110.9 (1.0) | C(2)–C(3)–C(4)    | 121.5 (1.9) |
| C(13)–C(8)–C(9)   | 117.7 (1.7) | C(3)–C(4)–C(5)    | 123.5 (2.2) |
| C(8)–C(9)–C(10)   | 119.1 (1.8) | C(4)–C(5)–C(6)    | 113.6 (2.1) |
| C(9)–C(10)–C(11)  | 122.9 (1.8) | C(5)–C(6)–C(1)    | 126.5 (1.7) |

is evident from Fig. 2. In perfect octahedral coordination all bond lengths involving a metal ion should be equal, the angles at the metal ion should be  $90^\circ$  and in this case, the cobalt ion should lie on the plane passing through Cl(2), N(6), O(2) and N(3) and also on the plane passing through Cl(1), N(3), O(1) and N(6). The best planes through the above two sets of atoms with deviations of the constituent atoms and the Co ion from them are given in Table 7.

### (ii) Bond lengths and angles in the ligand molecule

Bond lengths and their standard deviations are shown in Fig. 1(a). Average bond lengths of the present Co complex are given in Table 5 and compared with those of other metal complexes. Besides the comparison shown in Table 5 the average C-Cl bond length of  $1.764 \pm 0.017 \text{ \AA}$  is also in very good agreement with  $1.76 \pm 0.03 \text{ \AA}$  observed in 1,5-dichloronaphthalene (Kitaigorodskii & Kabalkina, 1951) and  $1.755 \pm 0.005 \text{ \AA}$  in carbon tetrachloride (Hassel & Viervoll, 1947). The observed average N-CH<sub>3</sub> bond  $1.43 \text{ \AA}$  and the average C-C bond in the benzene ring  $1.409 \text{ \AA}$  are in close agreement with  $1.426 \pm 0.012 \text{ \AA}$  and  $1.395 \pm 0.005 \text{ \AA}$  respectively as reported in *International Tables for X-ray Crystallography* (1968). The average N-N bond of  $1.318 \text{ \AA}$  is comparable with that in the cobalt(III) derivative of 1,3-diphenyltriazene(1) (Table 5).

The standard deviations in bond angles are derived from the standard deviations of the atomic coordinates (Darlow, 1960). Bond angles are shown in Fig. 1(b) and are listed in Table 6 with their standard deviations.

### (iii) Geometry of the molecule

Each of the two ligands of the present complex may be considered as roughly planar (Fig. 4). Best planes passing through these ligands are shown in Fig. 5,

where deviations of the atoms from the planes are also indicated. The equations of these planes are given in Table 7. It is found that the three constituent parts of a ligand *i.e.* the phenyl ring, the triazene ring and the group of atoms bridging these two (indicated as C, A and B for one ligand and F, D and E for the other in

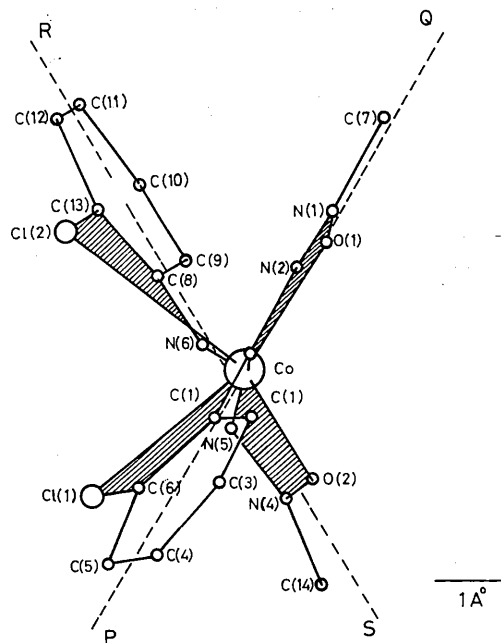


Fig. 5. Lines  $PQ$  and  $RS$  are intersections of the best planes passing through each ligand with the plane of the paper. The diagram shows each ligand as it appears when looked at parallel to the corresponding best plane and perpendicular to the lines  $PQ$  and  $RS$ . The scale for deviation of atoms from the corresponding plane is given. The shaded parts correspond to planes  $A, B, D$  and  $E$  of Fig. 4.

Table 7. Equations of the best planes and deviations of constituent atoms from them

(Equation of the plane  $lx + my + nz = p$ , where  $x, y, z$  are the coordinates in  $\text{\AA}$ ,  $p$  is the perpendicular distance of the plane from origin and  $l, m, n$  are direction cosines of the normal).

| Plane                                  | $l$     | $m$    | $n$     | $p$                 | Constituent atoms and their deviations in $\text{\AA}$ |        |       |        |       |        |
|--|---------|--------|---------|---------------------|--|--------|-------|--------|-------|--------|
| Through ligand 1                       | -0.0108 | 0.8901 | -0.4556 | 1.9539 $\text{\AA}$ | Co   | 0.023  | N(1)  | -0.037 | N(2)  | 0.031  |
| Through ligand 2                       | -0.2398 | 0.8052 | 0.5424  | 1.9263              | N(3)   | 0.103  | C(7)  | -0.058 | O(1)  | 0.031  |
| A                                      | 0.0614  | 0.8645 | -0.4988 | 1.8250              | Co   | 0.062  | N(3)  | -0.165 | Cl(1) | 0.089  |
| B                                      | -0.0771 | 0.7428 | -0.6650 | 1.2965              | C(6)   | 0.125  | Cl(1) | -0.206 | C(3)  | -0.002 |
| C                                      | -0.2667 | 0.7810 | -0.5647 | 0.7560              | C(1)   | 0.001  | C(2)  | 0.001  | C(3)  | -0.002 |
| D                                      | -0.4955 | 0.6710 | 0.5516  | 1.630               | C(5)   | -0.004 | C(6)  | -0.060 | C(4)  | 0.035  |
| E                                      | -0.1441 | 0.6385 | 0.7560  | 1.76                | Co   | -0.002 | O(2)  | 0.064  | N(4)  | 0.002  |
| F                                      | 0.0025  | 0.8016 | 0.5978  | 1.4531              | N(5)   | 0.108  | N(6)  | 0.216  | C(14) | -0.115 |
| Through Cl(1), N(3), O(1), N(6) and Co | -0.1479 | 0.7432 | -0.6525 | 0.9958              | Co   | 0.150  | N(6)  | -0.231 | C(8)  | 0.042  |
| Through Cl(2), N(6), O(2), N(3) and Co | -0.2310 | 0.6456 | 0.7278  | 1.5622              | C(13)  | 0.172  | Cl(2) | -0.160 | C(10) | -0.025 |
|  |         |        |         |                     | C(8)   | -0.021 | C(9)  | 0.062  | C(13) | -0.052 |
|  |         |        |         |                     | C(11)  | 0.026  | C(12) | 0.009  |       |        |
|  |         |        |         |                     | Co   | 0.323  | Cl(1) | -0.048 | N(3)  | -0.044 |
|  |         |        |         |                     | O(1)   | -0.105 | N(6)  | -0.081 |       |        |
|  |         |        |         |                     | Co   | 0.288  | Cl(2) | -0.089 | N(6)  | 0.055  |
|  |         |        |         |                     | N(3)   | -0.038 | O(2)  | -0.157 |       |        |

Fig. 4) are individually very nearly planar. Equations for these planes and deviations of constituent atoms are also listed in Table 7. It may be noted that the

planes *A* and *B* appear to be bent toward the chlorine atom of the other ligand and *vice-versa* (Fig. 5).

#### (iv) Packing

The packing of the molecules in the crystal is illustrated in Fig. 6 as viewed along the *c* axis. Molecules numbered I, II, III and IV correspond to symmetrically equivalent positions (Table 8). The nearest intermolecular approach is 3.34 Å between O(2) of molecule I and C(12) of molecule IV. Other short intermolecular distances are shown in Fig. 6 and have been listed in Table 8 for atoms other than hydrogen. It may be concluded from these distances that the molecular packing is very good.

#### (v) Thermal vibrations

The thermal parameters, listed in Table 3, imply the almost isotropic motion of Co, O(1) and O(2). The isotropic *B* for these atoms ranges from 3.5 to 4.3 Å<sup>2</sup>. Larger thermal vibrations are found for atoms N(1), N(2), C(4) and C(14) with *B* ranging from 5.4 to 6.2 Å<sup>2</sup>; whereas small vibrations are observed for N(5), C(1) and C(8) with *B* varying from 2.4 to 2.8 Å<sup>2</sup>. The average value of *B* for all atoms other than hydrogen is 4.1 Å<sup>2</sup>.

Anisotropic thermal vibrations have been interpreted in terms of thermal ellipsoids. The magnitudes and the direction cosines of the principal axes of the thermal ellipsoids have been calculated for all atoms and have been plotted in Fig. 7. It may be pointed out that, only because an approximate absorption correction, as indicated earlier, was applied to the data, this approximation as well as any other systematic error will be reflected in the values of the thermal parameters (Sri-

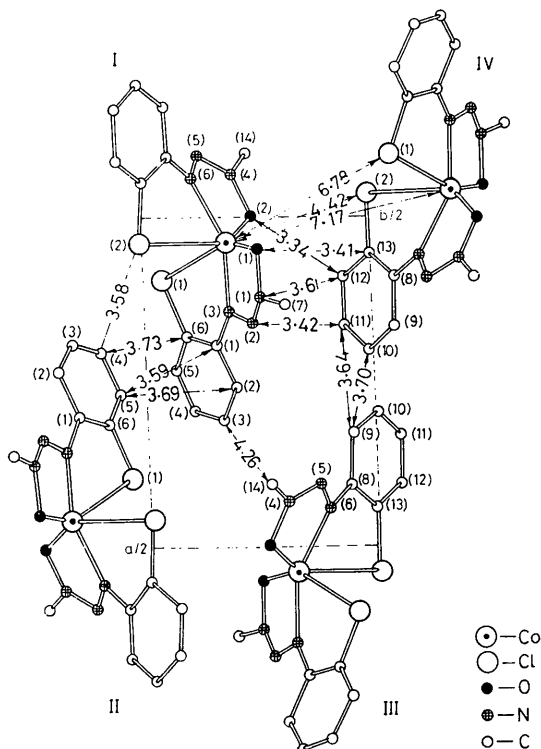


Fig. 6. Packing of the molecules of bis-(1-methyl-3-*o*-chlorophenyltriazeno)cobalt(II) in the crystal. Short intermolecular approach-distances are shown.

Table 8. Intermolecular distances less than 4 Å

Symmetrically equivalent points in the unit cell.

| Atom (in molecule I) | To atom | In molecule | Distance | Atom (in molecule I)   | To atom | In molecule | Distance |
|----------------------|---------|-------------|----------|------------------------|---------|-------------|----------|
| Co                   | C(12)   | IV          | 3.64 Å   | C(2)                   | C(5)    | II          | 3.70 Å   |
| O(1)                 | Cl(2)   | IV          | 3.73     |                        | C(14)   | III         | 3.91     |
|                      | C(8)    | IV          | 4.03     |                        | C(11)   | IV          | 3.80     |
|                      | C(11)   | IV          | 3.99     | C(3)                   | C(5)    | II          | 3.91     |
|                      | C(12)   | IV          | 3.42     | C(4)                   | C(5)    | II          | 4.00     |
|                      | C(13)   | IV          | 3.41     | C(5)                   | C(5)    | II          | 3.97     |
| O(2)                 | C(12)   | IV          | 3.34     | C(6)                   | C(4)    | II          | 3.73     |
| N(1)                 | C(8)    | IV          | 3.98     |                        | C(5)    | II          | 3.65     |
|                      | C(10)   | IV          | 3.86     | C(7)                   | C(8)    | IV          | 3.80     |
|                      | C(11)   | IV          | 3.70     |                        | C(9)    | IV          | 3.85     |
|                      | C(12)   | IV          | 3.61     |                        | C(10)   | IV          | 3.98     |
|                      | C(13)   | IV          | 3.71     |                        |         |             |          |
| N(2)                 | C(10)   | IV          | 3.70     | Atom (in molecule III) |         |             |          |
|                      | C(11)   | IV          | 3.43     |                        |         |             |          |
|                      | C(12)   | IV          | 3.70     |                        |         |             |          |
| N(3)                 | C(11)   | IV          | 3.52     | C(9)                   | C(10)   | IV          | 3.70     |
|                      | C(12)   | IV          | 3.64     |                        | C(11)   | IV          | 3.64     |
| C(1)                 | C(4)    | II          | 3.86     | C(10)                  | C(10)   | IV          | 4.03     |
|                      | C(5)    | II          | 3.59     |                        | C(11)   | IV          | 3.77     |
|                      | C(11)   | IV          | 3.85     |                        |         |             |          |



vastava & Lingafelter, 1966). Therefore the relative magnitudes and directions rather than the values of the root mean square amplitudes determined from the present study are of significance. The values for the cobalt and chlorine atoms have also been listed in Table 9. It may be noted that the Cl(1) and Cl(2) have maximum amplitudes of vibration approximately in the direction of the normal to the planes B and E (Fig. 7).

Table 9. The direction cosines ( $l_1$ ,  $l_2$ ,  $l_3$ ) of the principal axes of thermal ellipsoids relative to the crystal axes and the root mean square vibrational displacements in Å for cobalt and chlorine atoms

| Atom  | R.m.s. displacement | $l_1$   | $l_2$  | $l_3$   |
|-------|---------------------|---------|--------|---------|
| Co    | 0.2416              | -0.3236 | 0.6213 | 0.7136  |
|       | 0.2240              | -0.2102 | 0.6882 | -0.6944 |
|       | 0.1776              | 0.9225  | 0.3747 | 0.0921  |
| Cl(1) | 0.2998              | 0.0468  | 0.5648 | -0.8239 |
|       | 0.2338              | -0.8782 | 0.4163 | 0.2355  |
|       | 0.1637              | 0.4760  | 0.7125 | 0.5154  |
| Cl(2) | 0.3268              | 0.0179  | 0.6219 | 0.7829  |
|       | 0.2159              | 0.3471  | 0.7304 | -0.5882 |
|       | 0.1658              | -0.9376 | 0.2823 | -0.2028 |

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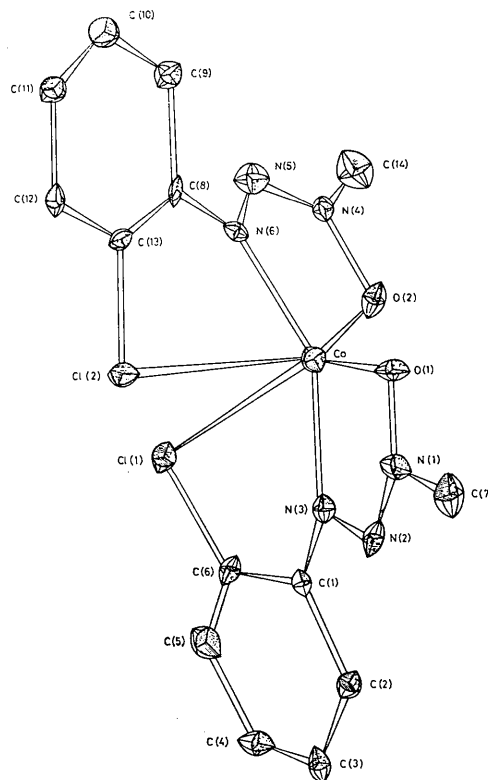


Fig. 7. A view of the anisotropic thermal vibrations of the atoms (Dwivedi, 1970).