approximate $C_2$ molecular symmetry with the coordination square distorted towards a tetrahedral geometry.

The unique molecular conformation in the Pd$^{II}$ case is very similar to the $C_i$ molecule in the Cu$^{II}$ case. The salicylideneaminato group is planar (within 0·16 Å), but its least-squares plane does not coincide with the least-squares coordination plane, the dihedral angle being 27·0 (5)°. The N-bonded phenyl group is planar (within 0·013 Å) and tilted by 58·1 (2)° with respect to the salicylideneaminato plane. Not very different values were found for the Cu$^{II}$ homologue [46 (2)° for the $C_i$ molecule; 66 (2) and 57 (2)° for the other]. Unlike the Cu$^{II}$ complex, the conformation of the alkoxy groups in the Pd$^{II}$ compound is very close to all-*trans* and no evidence of statistical disorder was detected. The main axes are roughly parallel. The packing indeed seems rather tighter in the Pd$^{II}$ case since the molecular volume is 1243 (1) Å$^3$ for Pd$^{II}$ and 1264 (1) Å$^3$ for Cu$^{II}$. Evaluation of the central ellipsoid of inertia for the whole molecule (equal weights for all non-H atoms were considered) results in a mean square displacement from the principal plane of inertia of 0·67 (2) Å with a maximum of 1·81 (2) Å for atom C4. The molecular packing along the z axis is characterzied by a sequence of molecular layers containing molecules with their elongation axes (*i.e.* the major axis of the central ellipsoid of inertia of the molecule) mutually parallel but tilted by 73 (1)° with respect to the xy plane. No interdigitation of the alkoxy terminals belonging to contiguous layers is observed, while this feature is present to a small extent in the crystal packing of the Cu$^{II}$ homologue. The packing along the y axis within each of the layers is characterized by an alternate sequence at $y = 0$ and $y = \frac{1}{2}$ of rows of molecules with different orientation. Each row contains strictly parallel molecules while molecules belonging to contiguous rows have their average planes mutually orthogonal.

The shortest metal–metal distance, 5·961 (5) Å, is found between contiguous molecules of the same row. This value is ~1 Å shorter than the shortest Cu–Cu distance measured for the Cu$^{II}$ homologue.

### References

CARUSO, U., ROVIELLO, A. & SIRIGU, A. (1988). *Liq. Cryst.* In the press.

Enraf–Nonius (1981). *Structure Determination Package.* Enraf–Nonius, Delft, Holland.

GHEDINI, M., LICOCCIA, S., ARMENTANO, S. & BARTOLINO, R. (1984). *Mol. Cryst. Liq. Cryst.* **108**, 269–275.

GHEDIN, M., LONGERI, M. & BARTOLINO, R. (1982). *Mol. Cryst. Liq. Cryst.* **84**, 207–211.

GHEDINI, M., PELLEGRINO, C., ARMENTANO, S., DE MUNNO, G. & BRUNO, G. (1986). *Inorg. Chim. Acta,* **122,** 193–198.

IANNELLI, P., IMMIRZI, A., ROVIELLO, A. & SIRIGU, A. (1988). *Liq. Cryst.* **3**, 115–122.

*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

OHTA, K., MUROKI, H., TAKAGI, A., HATADA, K., EMA, H., YAMAMOTO, I. & MATSUZAKI, K. (1986). *Mol. Cryst. Liq. Cryst.* **140**, 131–152.

OVCHINNIKOV, I. V., GALYAMETDINOV, YU. G., IVANOVA, G. I. & YAGFAROVA, L. M. (1984). *Dokl. Akad. Nauk SSSR,* **276**, 126–128.

SADASHIVA, B. K. & RAMESHA, S. (1986). *Mol. Cryst. Liq. Cryst.* **141**, 19–24.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

# Structure of Chloro(nitrilotriethanolato)cobalt(II)

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**Abstract.** [Co(C$_6$H$_{14}$NO$_3$)Cl], $M_r = 242·6$, orthorhombic, *Pnma,* $a = 16·893$ (7), $b = 7·890$ (2), $c = 6·792$ (2) Å, $V = 905$ Å$^3$, $Z = 4$, $D_x = 1·76$ g cm$^{-3}$, Cu $K\alpha$, $\lambda = 1·5418$ Å, $\mu$(Cu $K\alpha$) $= 50·6$ cm$^{-1}$, $F(000) = 492$, room temperature, final $R = 0·076$, $wR = 0·081$ for 720 unique reflections. The triethanolamine ligand

acts as a quadridentate ligand and forms a monomeric structure of five-coordinated cobalt, exhibiting an approximate trigonal bipyramidal geometry around Co. The crystal packing is through hydrogen bonds and van der Waals interactions.

**Introduction.** Triethanolamine has been used as a coordinating ligand with a number of metal ions. Considerable work has been done on the behaviour of metal complexes in solution, but little is known of these complexes in the solid state (Hieber & Levy, 1934; Duff & Steer, 1932). Examination of these complexes in the solid state by magnetic, spectroscopic and X-ray powder techniques, independently by Hughes & Rutt (1968) and Kuge & Yamato (1969), led to significant conclusions about their stoichiometry and stereochemistry.

On the basis of electron spectroscopy, it was found that the spectra obtained for $[Co\{N(CH_2CH_2OH)_2-(CH_2CH_2O)\}X]$ ($X = Cl^-$, $Br^-$, $NCS^-$) cannot be consistently explained in terms of tetrahedral or octahedral configuration. The spectra are similar to those obtained for five-coordinated high-spin cobalt(II) complexes. The magnetic moments of the complexes are also in the range of five-coordinated $Co^{II}$ complexes with a ligand of this type. Thus it can be presumed that cobalt in $[Co\{N(CH_2CH_2OH)_2-(CH_2CH_2O)\}X]$ ($X = Cl^-$, $Br^-$, $NCS^-$) complexes is five coordinated (Ciampolini, Nardi & Speroni, 1966; Ciampolini & Nardi, 1967; Ciampolini & Nardi, 1966). Based on these studies and comparisons with similar structures of $Ni^{II}$ (Nielsen, Hazell & Rasmussen, 1972; Ramalingam, 1986) it is expected that the ligand triethanolamine is terdentate rather than quadridentate and hence the most probable configuration is polynuclear cobalt with bridging oxygens of the alcoholate group. Any final conclusion about the precise configuration requires a complete three-dimensional X-ray crystal structure analysis, which was undertaken here.

**Experimental.** Single crystals were obtained by the following procedure: 25 ml of 0·1 M cobalt nitrate, 25 ml of 0·1 M cobalt chloride and 25 ml of 0·2 M triethanolamine solutions in methanol were mixed with 10 ml of water and the system kept aside undisturbed. After fifteen days, single crystals were formed, which were washed from adherent viscous solution with methanol, air dried and kept over concentrated sulfuric acid. Unit-cell dimensions of a single crystal 0·03 × 0·02 · 0·53 mm were obtained from the least-squares refinement of $\theta$ values of 25 high-angle ($10 < \theta < 20°$) reflections. From the systematic absences ($0kl$: $k+l = 2n+1$, $hk0$: $h = 2n+1$, $0k0$: $k = 2n+1$) the space group could be either $Pnma$ or $Pna2_1$. Three-dimensional intensity data collected on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Cu $K\alpha$ radiation. $\omega/2\theta$ scan mode.

835 reflections in the range $2 < \theta < 70°$ ($h$: 0 to 20, $k$: 0 to 9, $l$: 0 to 8) measured, 720 of which considered observed $[I > 3\sigma(I)]$. Maximum counting time for each reflection 60 s. Standard reflections ($10\bar{6}$ and $01\bar{7}$) measured periodically, no significant change in intensity. Absorption correction (max. 0·85 and min. 0·30) was applied using the program $ABSORB$ (Ugozzoli, 1987). Data analysed in the noncentrosymmetric space group $Pna2_1$ did not reveal the structure. Next, the centrosymmetric $Pnma$ was tried using a Patterson map and difference Fourier maps which gave the structure. Refinement by least squares using $SHELX76$ (Sheldrick, 1976), $\sum |\Delta F|^2$ minimized. C atoms attached to the N atom, namely C(2) and C(3), showed large thermal motions and hence were considered to be disordered. C(2) which lies on the mirror plane was instead given two positions, C(2) and C(2′), related by the mirror, with an occupancy of 0·5. C(3) which lies in a general position was given two positions, C(31) and C(32), again with a fractional occupancy of 0·5. Disordered C atoms were isotropically refined. Maximum peak height in final difference Fourier map $< 1$ e $\text{Å}^{-3}$, (shift/e.s.d.)$_{max}$ in final refinement cycle was 0·024. Atomic scattering factors for atoms from Cromer & Mann (1968) and anomalous-dispersion corrections from Cromer & Liberman (1970). Weighting scheme $w = 1/[\sigma^2(F_o) + 0·0002|F|^2]$. Final $R = 0·076$, $wR = 0·081$ for 720 unique reflections. These rather high $R$ values seem to be due to disorder effects.

**Discussion.** The fractional coordinates of all the atoms, with equivalent isotropic thermal parameters, are given in Table 1.* An $ORTEP$ plot (Johnson, 1965) of the molecule is shown in Fig. 1. The relevant bond lengths and bond angles are given in Table 2.

From crystallographic considerations, Co, Cl, N and the ethanolate group must lie on a mirror plane and the two ethanol groups should be mirror related to each other. Due to disorder, C(2) is shifted away from the mirror plane and the single carbon C(3) occupies two positions, namely C(31) and C(32). The geometry around cobalt can be best described as an approximate trigonal bipyramid with two O atoms from the two ethanol groups and one from the ethanolato group forming the basal plane and chlorine and nitrogen occupying the apical positions.

Co—Cl and Co—N distances of 2·302 (3) and 2·150 (8) Å are normal and show strong covalent interaction of chlorine and nitrogen with cobalt. The N—Co—Cl angle of 177·9 (3)° shows that the three atoms are nearly linear.

Table 1. *Final fractional atomic coordinates* ($\times 10^4$ *for* Co *and* Cl *and* $\times 10^3$ *for others*) *and equivalent isotropic thermal parameters* ($\times 10^4 \, \text{Å}^2$ *for* Co *and* $\times 10^3$ *for others*) *with estimated standard deviations in parentheses*

$$U_{eq} = \frac{1}{3} \sum_{i=1}^{3} U_{ii}.$$

|  | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Co | 2253 (1) | 2500 | 2518 (3) | 236 (8) |
| Cl | 3570 (2) | 2500 | 3391 (5) | 29 (1) |
| N | 101 (1) | 250 | 181 (1) | 18 (4) |
| O(1) | 236 (1) | 250 | −37 (1) | 20 (3) |
| C(1) | 160 (1) | 250 | −143 (2) | 33 (7) |
| C(2) | 96 (1) | 308 (1) | −26 (2) | 24 (3) |
| C(31) | 73 (1) | 424 (2) | 203 (2) | 26 (3) |
| C(32) | 61 (1) | 369 (2) | 318 (2) | 28 (3) |
| O(2) | 190 (1) | 471 (1) | 384 (1) | 25 (2) |
| C(4) | 109 (1) | 513 (1) | 366 (1) | 43 (5) |

Table 2. *Bond lengths* (Å) *and bond angles* (°)

| | | | |
|---|---|---|---|
| Co—Cl | 2·303 (3) | Co—N | 2·150 (8) |
| Co—O(1) | 1·975 (9) | Co—O(2) | 2·048 (5) |
| N—C(31)* | 1·45 (1) | N—C(2) | 1·49 (1) |
| N—C(32)* | 1·48 (1) | C(4)—O(2) | 1·42 (1) |
| C(3)—C(4)* | 1·48 (2) | C(1)—O(1) | 1·46 (1) |
| C(2)—C(1) | 1·43 (1) | | |

| | | | |
|---|---|---|---|
| Cl—Co—N | 177·8 (3) | O(1)—Co—Cl | 99·7 (2) |
| O(1)—Co—N | 82·5 (3) | O(2)—Co—Cl | 99·4 (2) |
| O(2)—Co—N | 79·6 (2) | O(1)—Co—O(2) | 117·6 (2) |
| O(2)—Co—O(2′)† | 116·9 (2) | Co—O(1)—C(1) | 114 (1) |
| Co—O(2)—C(4) | 116·2 (5) | O(1)—C(1)—C(2) | 113 (1) |
| O(2)—C(4)—C(31) | 110·5 (9) | C(1)—C(2)—N | 112 (1) |
| O(2)—C(4)—C(32) | 112·0 (9) | Co—N—C(2) | 105 (1) |
| C(4)—C(31)—N | 113 (1) | | |
| C(4)—C(32)—N | 113 (1) | | |
| Co—N—C(31) | 106 (1) | | |
| Co—N—C(32) | 107 (1) | | |

\* C(31) and C(32) are the disordered C(3) positions.
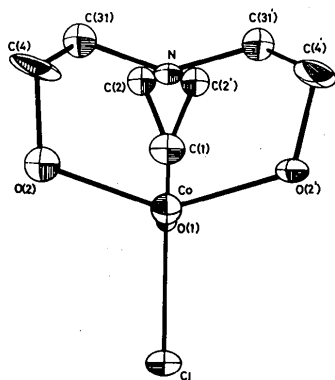† O(2′) is mirror related to O(2).



Fig. 1. Perspective view of the molecule. The disordered positions C(32) and C(32′) are omitted for clarity.

The shorter Co—O bond length [1·975 (9) Å] is attributed to the negative charge on the O atom in the $C_2H_4O^-$ group. In this compound, the ligand acts as a quadridentate ligand, as was predicted for chloro-triethanolaminatozinc(II) on the basis of infrared spectra (Sen & Dotson, 1970). Earlier work on the crystal structure of the ligand in $Ni(tea)_2(NO_3)_2$ (tea = triethanolamine (Nielson, Hazell & Rasmussen, 1972) and $Ni(tea)_2RSSR$ ($RSSR$ = dithiosalicylate) (Ramalingam, 1986) report the ligand to be terdentate.

The base angles of the equatorial plane are close to 120°, thus approximating to $C_3$ symmetry. The average O—Co—O, O—Co—Cl and O—Co—N angles are 117·4 (2), 99·5 (2) and 80·6 (2)° respectively. The Co atom does not lie in the plane of O atoms but is shifted towards the Cl atom, the deviation from the plane being 0·249 (2) Å.

The geometry around nitrogen can be approximated to that of a tetrahedron. The bond parameters around nitrogen show deviation from normal values due to the disorder exhibited by the C atoms attached to it.

In conclusion, the triethanolamine ligand acts as a quadridentate ligand and forms a monomeric structure of five-coordinated cobalt exhibiting an approximate trigonal bipyramidal geometry.

The hydroxyl groups of the neighbouring molecules approach each other to within a range of 2·4–2·8 Å indicating the presence of hydrogen bonding. The crystal packing is governed by these hydrogen bonds, and van der Waals interactions.

**References**

CIAMPOLINI, M. & NARDI, N. (1966). *Inorg. Chem.* **5**, 1151–1154.
CIAMPOLINI, M. & NARDI, N. (1967). *Inorg. Chem.* **6**, 445–449.
CIAMPOLINI, M., NARDI, N. & SPERONI, G. P. (1966). *Coord. Chem. Rev.* **1**, 222–233.
CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.
DUFF, J. C. & STEER, E. H. (1932). *J. Chem. Soc.* pp. 2861–2862.
HIEBER, W. H. & LEVY, E. (1934). *Z. Anorg. Allg. Chem.* **219**, 225–237.
HUGHES, M. N. & RUTT, K. J. (1968). *J. Chem. Soc. A*, pp. 2788–2790.
JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
KUGE, Y. & YAMATO, S. (1969). *Bull. Chem. Soc. Jpn*, **42**, 2552–2555.
NIELSEN, K., HAZELL, R. G. & RASMUSSEN, S. E. (1972). *Acta Chem. Scand.* **26**, 889–896.
RAMALINGAM, K. (1986). PhD Thesis, Indian Institute of Technology, Madras, India.
SEN, B. & DOTSON, R. L. (1970). *J. Inorg. Nucl. Chem.* **32**, 2707–2716.
SHELDRICK, G. M. (1976). *SHELX76.* Program for crystal structure determination. Univ. of Cambridge, England.
UGOZZOLI, F. (1987). *Comput. Chem.* **11**(2), 109–120.