

In the first least-squares refinements of the structures the thermal parameters of the atoms C(30), C(31), C(33) and C(34) of one phenyl ring were very large. The peaks in the difference maps of the above atoms were elongated perpendicular to the plane of the phenyl group indicating two alternative positions obtained by a small rotation around an axis through C(29) and C(32) (Fig. 1a and b). A least-squares refinement with two alternative rings C(29A)—C(34A) and C(29B)—C(34B), both with the site occupancy factor 0.5, gave a satisfactory result.

The packing of the molecules is shown in Fig. 3. In the structures there are layers of anions and cations parallel to the (100) planes. The shortest intermolecular distances are I—H(33B) 2.93 (2) Å, Cl—H(33B) 2.73 (1) Å, and the shortest C—H contact between an anion and a cation is 2.62 (1) Å. The H atoms have, however, been generated geometrically.

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**Structures of Pentaammine(5-cyanotetrazolato- N^2)cobalt(III) Perchlorate (CP),
[Co(C₂N₃)(NH₃)₅](ClO₄)₂, and (5-Amidinetetrazolato- N^1, N^5)tetraamminecobalt(III)
Bromide (ATCB), [Co(C₂H₃N₆)(NH₃)₄]Br₂***

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Abstract. CP: $M_r = 437.04$, $F(000) = 888$, monoclinic, $P2_1/a$, $a = 24.813$ (5), $b = 7.661$ (2), $c = 7.971$ (1) Å, $\beta = 101.17$ (1)°, $V = 1486.5$ Å³, $Z = 4$, $D_m = 1.989$ (2), $D_x = 1.952$ (1) Mg m⁻³, Mo K α , $\lambda = 0.71069$ Å, $\mu = 1.598$ mm⁻¹, room temperature, $R = 0.081$ on 1937 unique reflections; ATCB: $M_r = 397.96$, $F(000) = 388$, triclinic, $P1$, $a = 7.450$ (6), $b = 13.471$ (5), $c = 7.130$ (5) Å, $\alpha = 96.23$ (6), $\beta = 117.30$ (7), $\gamma = 79.51$ (6)°, $V = 625.0$ Å³, $Z = 2$, $D_x = 2.114$ (1), $D_m = 2.101$ (2) Mg m⁻³, Mo K α , $\lambda = 0.71069$ Å, $\mu = 7.642$ mm⁻¹, room temperature, $R = 0.049$ on 2120 reflections. Crystals of CP are radiation-sensitive. Both structures determined from Patterson

and Fourier syntheses and refined by least-squares methods. In CP, the Co atom is octahedrally coordinated to ammine groups (1.96–1.99 Å) and a tetrazole-ring N (1.92 Å); in ATCB the Co—ammine distances range in a similar manner (1.95–1.98 Å) while those to the chelate-ring N atoms are 1.91 and 1.94 Å. In CP, one of the perchlorate groups is disordered resulting in a model with five O positions (Cl—O distances: 1.34–1.44 Å) while those for the other ClO₄⁻ ion correspond to the expected tetrahedron (1.40–1.44 Å). In both compounds, the coordinated Co-complex ions and the anions form layers. Hydrogen-bonded networks link these anions to the Co³⁺ ions *via* the ammine groups.

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Introduction. A hot bridgewire is a common method used to ignite a non-primary explosive. In deflagration-

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to-detonation transition-type devices after ignition the explosive deflagrates with increasing velocity resulting in a shock wave and subsequent detonation. One material which exhibits such properties is CP. This material has found application in detonators because it is spark-insensitive as a loose powder which results in increased safety in handling relative to primary explosives. In order to understand the behavior of such materials, it is important to identify and understand the behavior of impurities. One such possible impurity in CP is an amidine chelate, (5-amidinotetrazolato)-tetraamminecobalt(III) perchlorate, which could possibly form in a solid-state reaction from CP. The bromide derivative of this material, ATCB, serves as a convenient material to determine the nature of the chemical bonding of the chelated cobalt.

Experimental. Crystals were obtained from aqueous solution by controlled evaporation in a desiccator; the morphologies appear to be consistent with point-group symmetries $2/m$ for CP and $mm2$ for ATCB; however, subsequent precession photographs reveal $mm2$ to be the pseudosymmetry resulting from twinning as found for the majority of the crystals; the actual point symmetry for ATCB is $\bar{1}$ as determined on a carefully selected, untwinned specimen. Densities were determined by a pycnometer. The data crystals were approximately equidimensional with maximum dimensions of 0.34mm (CP) and 0.18mm (ATCB) so that absorption corrections would be unnecessary. Precession and Weissenberg photographs used to determine preliminary unit-cell dimensions and space-group extinctions; for CP such photographs also used to monitor crystal perfection. CP appears to suffer radiation damage as revealed by growth of streaks and broadening of diffraction spots with time; crystals mounted, but not subjected to the X-ray beam were stable; four separate crystals used for intensity measurements, each data set scaled with respect to the standard reflections as a function of exposure time. Lattice parameters obtained by least squares from strong high- 2θ reflections (CP 22; ATCB 24). The θ - 2θ scan technique on a Picker diffractometer used our previously described experimental procedure (Graeber & Morosin, 1974); reflections within a hemisphere limited by $2\theta = 50^\circ$ measured with a β filter (Zr); three standard reflections were measured for each compound, with intensity variations of 10% for CP and 5% for ATCB; background radiation measured at each end of the scan (CP 2.4° ; ATCB, 2.8°) with crystal and counter stationary, and assumed to be a linear function of 2θ between these points; measured reflections: 7968 with $R_{\text{int}} = 0.083$ for CP, 2131 for ATCB; for CP/ATCB, 382/567 reflections less than 3σ and hence considered unobserved; $\sigma = (N_{\text{sc}} + K^2 N_b)^{\frac{1}{2}}$, where $N_{\text{s.c.}}$, N_b and K are the total scan counts, background counts and the time ratio of scan to background,

respectively. Intensities corrected for Lorentz and polarization effects, no corrections for absorption or extinction applied. Atomic scattering factors taken from the numerical Hartree-Fock wavefunctions of Cromer & Mann (1968); dispersion corrections from *International Tables for X-ray Crystallography* (1962). Fourier syntheses together with the least-squares procedure used to obtain the positions of the lighter N and O atoms; H positions not clearly defined on final Fourier syntheses and were not included in any refinement models. In CP, one of the perchlorate ions appeared disordered, showing five irregular maxima; one peak consistently larger than the remaining four; after several attempts failed to fit these maxima with perfectly tetrahedral ClO₄⁻ groups, an approximate, assumed model was chosen which consisted of assigning population parameters equal to $\frac{3}{4}$ for O(5), O(7), O(8) and O(9) and 1 to O(6). $\sum w(F_o - F_c)^2$ minimized with $w = n/\sigma^2$, where n = the number of symmetry equivalents or observations of a particular reflection; anisotropic thermal parameters refined; for CP, $wR = 0.092$ and $S = 1.24$; for ATCB, $wR = 0.062$ and $S = 1.38$; the parameter shifts in the last cycle of refinement for both compounds all less than two-tenths of the standard deviations. For CP, the maximum/minimum height in the final difference Fourier map is 1.7 (adjacent to disordered perchlorate)/ $-0.7 \text{ e } \text{\AA}^{-3}$ and $0.8/-1.5$ (near Br atoms) $\text{e } \text{\AA}^{-3}$ for ATCB. All numerical calculations performed with the XRAY 76 system (Stewart, 1976).

Discussion. The final least-squares parameters are given in Table 1.* The values for the thermal parameters for O atoms around Cl(2) are only slightly larger than those associated with Cl(1) and this appears to justify our assumed model for the disorder about that perchlorate group.

Projections of the CP and ATCB structures are shown in Figs. 1 and 2, respectively. In both crystals, the coordinated cobalt complex ion forms alternate sheets with the anions being linked by a hydrogen-bonding network. These sheets are more complex in the case of ATCB with the tetrazolato ligands stacking against each other.

Fig. 3 summarizes the bond lengths and angles found in CP and ATCB. These values are similar to those reported in other cobalt ammine complexes (Ito, Marumo & Saito, 1972; Brennan, Davies, Garafalo & Gardner, 1978). The amidino cyclization results in the chelate ring system with slightly shorter Co-N distances than those found in CP. Even the metal-ammine distances are consistently shorter in ATCB suggesting

* Lists of structure factors and anisotropic thermal parameters for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38335 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final least-squares positional parameters and equivalent isotropic thermal parameters for CP and ATCB

$$U_{eq} = \frac{1}{3} (\text{trace of the orthogonalized } U_{ij} \text{ matrix}).$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} (Å ²)
(a) CP				
Co	0.1210 (1)	0.2705 (2)	0.2051 (2)	0.043 (1)
Cl(1)	0.0067 (1)	0.2393 (5)	0.6568 (4)	0.056 (2)
Cl(2)	0.2521 (1)	0.2832 (6)	0.7515 (5)	0.064 (2)
O(1)	0.0419 (5)	0.252 (2)	0.534 (2)	0.107 (10)
O(2)	0.0492 (6)	0.188 (2)	0.568 (2)	0.128 (11)
O(3)	0.0020 (5)	0.106 (2)	0.778 (2)	0.103 (9)
O(4)	0.0191 (5)	0.405 (2)	0.741 (2)	0.105 (10)
O(5)	0.1968 (8)	0.213 (3)	0.692 (3)	0.144 (18)
O(6)	0.2991 (6)	0.198 (2)	0.713 (2)	0.137 (13)
O(7)	0.2397 (9)	0.422 (4)	0.636 (3)	0.161 (21)
O(8)	0.2705 (9)	0.378 (4)	0.900 (3)	0.149 (20)
O(9)	0.234 (1)	0.193 (3)	0.874 (4)	0.196 (28)
N(1)	0.0395 (4)	0.259 (4)	0.163 (1)	0.051 (6)
N(2)	0.2023 (4)	0.290 (2)	0.243 (1)	0.062 (7)
N(3)	0.1223 (4)	0.122 (2)	0.002 (1)	0.060 (7)
N(4)	0.1134 (4)	0.475 (2)	0.063 (1)	0.063 (7)
N(5)	0.1261 (4)	0.063 (2)	0.351 (2)	0.075 (8)
N(6)	0.1206 (4)	0.426 (2)	0.405 (1)	0.069 (8)
N(7)	0.0843 (5)	0.622 (2)	0.080 (2)	0.087 (9)
N(8)	0.0911 (5)	0.740 (2)	-0.032 (2)	0.074 (8)
N(9)	0.1430 (4)	0.495 (2)	-0.064 (1)	0.111 (11)
N(10)	0.1681 (6)	0.807 (2)	-0.359 (2)	0.087 (10)
C(1)	0.1276 (6)	0.661 (2)	-0.116 (2)	0.054 (8)
C(2)	0.1505 (6)	0.745 (2)	-0.255 (2)	0.057 (8)
(b) ATCB				
Co	0.8715 (2)	0.2705 (1)	0.1539 (2)	0.021 (1)
Br(1)	0.7963 (2)	0.5937 (1)	0.1621 (2)	0.044 (1)
Br(2)	0.5505 (2)	0.2100 (1)	0.4740 (2)	0.033 (1)
N(1)	0.639 (1)	0.1937 (7)	0.016 (2)	0.033 (5)
N(2)	1.099 (2)	0.3483 (7)	0.293 (2)	0.033 (6)
N(3)	0.720 (2)	0.3656 (7)	0.277 (2)	0.045 (6)
N(4)	0.767 (2)	0.3524 (7)	-0.094 (1)	0.032 (5)
N(5)	0.994 (1)	0.1820 (7)	0.393 (1)	0.029 (5)
N(6)	1.030 (1)	0.1709 (7)	0.057 (1)	0.027 (5)
N(7)	1.069 (2)	0.1533 (7)	-0.112 (1)	0.033 (5)
N(8)	1.193 (2)	0.0671 (7)	-0.081 (1)	0.035 (6)
N(9)	1.238 (1)	0.0275 (7)	0.105 (1)	0.031 (5)
N(10)	1.224 (2)	0.0302 (7)	0.524 (1)	0.034 (5)
O(1)	1.135 (2)	0.0942 (8)	0.184 (2)	0.028 (6)
O(2)	1.119 (2)	0.1019 (9)	0.384 (2)	0.030 (6)

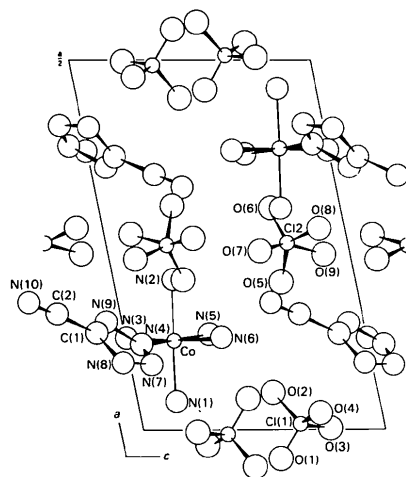


Fig. 1. Projection along [010] of one half unit cell of CP, *y* pointing out of the page.

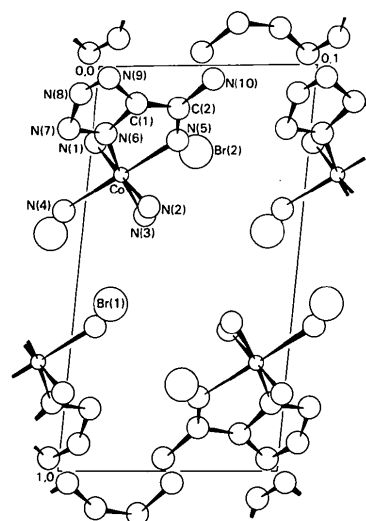


Fig. 2. View along [100] of the ATCB unit cell, *x* pointing out of the page.

metal-orbital involvement. In ATCB, the chelate ring and the tetrazolato ring are essentially planar (1.9° angle between the least-squares planes) with the Co atom on the plane. The rings are essentially normal (89.2°) to the plane through ammine N atoms 1,2,4 and 5. In CP, the tetrazolato ring is tipped with respect to the Co—N(4) bond so that the distance of Co to the least-squares plane is 0.13 \AA ; the cyano group is similarly tipped along the same side of this plane. Examination of the hydrogen-bonding scheme as well as other near-neighbor contacts [3.20 \AA is the closest nonbonding contact between N(10) and O(5)] does not suggest any obvious packing arguments consistent with such a 'bowing' of the Co—tetrazolato unit.

A probable hydrogen-bond network can be deduced for both structures by examining the interatomic separations and angles. In several cases, bifurcated bonds appear to be present, for example N(5) in ATCB and N(1) in CP. The remaining cases, with more than three near-neighbor contacts between ammine groups and neighboring electronegative atoms, also involve the disordered perchlorate ion.

The O atoms of both perchlorate groups have thermal parameters ($U_{eq} \geq 0.1 \text{ \AA}^2$) which on the average are significantly larger than those of the other atoms; those corresponding to the disordered perchlorate are somewhat larger than those for the ordered group. It is noteworthy that the thermal parameters for the light atoms are larger for CP than ATCB. This may be the consequence of the radiation damage in the CP crystals.

The high *R* value for our CP refinement probably results from the radiation damage suffered by this material. Mounted crystals are stable but rapidly degrade after several days of exposure to X-ray

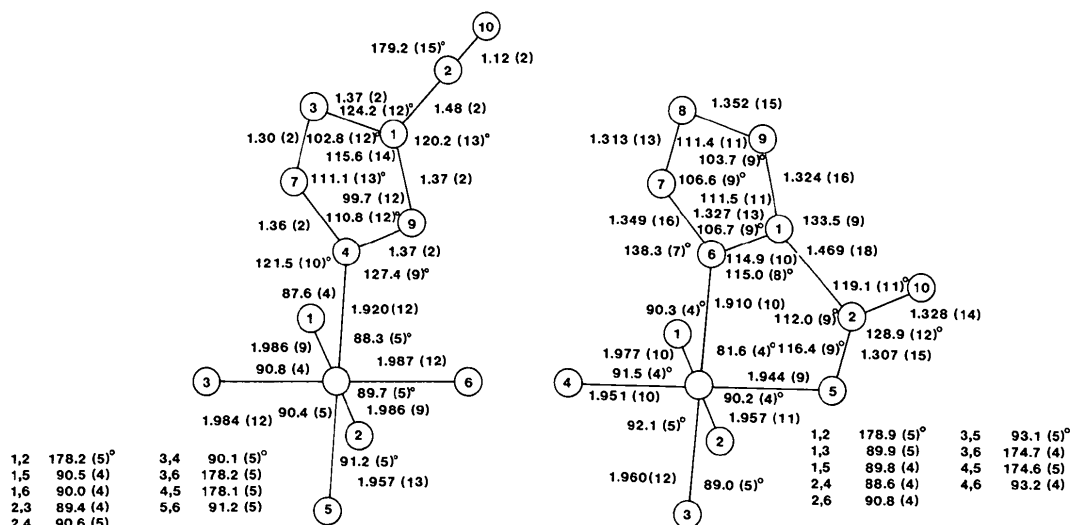


Fig. 3. Bond lengths (Å) and angles (°) for CP and ATCB. In CP, the Cl(1)—O(*i*) lengths are 1.40 (1), 1.44 (2), 1.43 (1) and 1.44 (1) Å for *i* = 1, 2, 3 and 4, respectively, and the Cl(2)—O(*i*) lengths are 1.47 (2), 1.42 (2), 1.40 (3), 1.39 (2) and 1.34 (3) Å for *i* = 5, 6, 7, 8 and 9, respectively. The O—Cl(1)—O angles range from 106.9 (8) to 111.2 (8)°; for O—Cl(2)—O, the unit-weight O(6) forms essentially tetrahedral angles to O(7), O(8) and O(9) while that to O(5) is large, 121 (1)°.

radiation. It is assumed that there is no relationship between damage and the disorder of the perchlorate group since many other perchlorates are known in which disorder is found, and no comment has been made concerning radiation damage.

The kinetics of imine cyclization, which requires conversion from 2-bonding of the properly substituted tetrazolato ligand to 1-bonding, may occur in solution and has been discussed by Harrowfield & Sargeson (1979). With care, both 2- and 1-bonded substituted tetrazolato materials can be crystallized. The conversion from 1- to 2-bonded (or 2- to 1-bonded) on substituted tetrazolato ligands lacking the cyano group has been examined by Ellis & Purcell (1981). Since CP exhibits 2-bonding to the ring whereas ATCB shows 1-bonding, it appears unlikely that the amidine chelate could form from CP in a solid-state reaction.

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Structure of Lithium 1-Pyrrolidinecarbodithioate Tetrahydrate, Li.C₅H₈NS₂.4H₂O

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Abstract. $M_r = 225.25$, monoclinic, $P2_1/n$, $a = 10.279$ (1), $b = 9.989$ (3), $c = 11.291$ (1), Å, $\beta = 93.03$ (1)°, $V = 1158$ (1) Å³, $Z = 4$, $D_m = 1.304$ (5), $D_x = 1.292$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.433$ mm⁻¹, $F(000) = 480$, $T = 298$ K, $R = 0.030$, $R_w = 0.041$ for 2680 intensities. Lithium coordinates

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