

Fig. 4. A unit cell (ORTEP; Johnson, 1976) of the title compound viewed from a direction nearly along the *a* axis. Four entire formula units are shown to illustrate the stacking along the *b* axis.

Fig. 4 is a stereoview of a unit cell for tetrasodium 1,4,5,8-naphthalenetetracarboxylate octahydrate viewed from a direction nearly along the *a* axis. The anions are stacked along the *b* axis and make an angle of 38.6° with the *ac* plane. The separation of corresponding atoms in adjacent anions within the stack is $8.144(3) \text{ \AA}$, the length of the *b* axis. The stacks are staggered such that the carboxyl anions do not line up with each other as they might in their acid forms. The sodium cations, by coordinating with the carboxyl anions, partially occupy the space between the organic portions of the structure, with the water molecules completing the sodium ion coordination polyhedra and filling the remaining space. The $\text{H}_2\text{O}(5)$ and $\text{H}_2\text{O}(6)$ water molecules are positioned between the carboxyl anions while the $\text{H}_2\text{O}(7)$ and $\text{H}_2\text{O}(8)$ water molecules are positioned between the naphthalene cores. The combined effect

of the close approaches, the anion-cation coordination and the hydrogen bonding is to cause the displacement parameters for the atoms in the present study to be significantly smaller than for typical organic structures. The average B_{eq} for the C and O atoms comprising the present structure is $1.4(2) \text{ \AA}^2$; the average B_{eq} for the C and O atoms of 1,8-naphthalenedicarboxylic acid, for example, is $4.1(7) \text{ \AA}^2$ (Fitzgerald, Gallucci & Gerkin, 1991).

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Structure of $[\text{CH}_3\text{TMPP}]_2\text{Co}_2\text{Cl}_6$ [$\text{CH}_3\text{TMPP} = \text{Tris}(2,4,6\text{-trimethoxyphenyl})\text{-methylphosphonium}$]

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Abstract. Tris(2,4,6-trimethoxyphenyl)methylphosphonium hexachlorodicobaltate(II), $2\text{C}_{28}\text{H}_{36}\text{O}_9\text{P}^+ \cdot \text{Co}_2\text{Cl}_6^{2-} \cdot 2\text{CH}_2\text{Cl}_2$ (1), $M_r = 1595.6$, triclinic, $P\bar{1}$, $a = 10.889(5)$, $b = 13.54(6)$, $c = 14.005(5) \text{ \AA}$, $\alpha = 63.45(3)^\circ$, $\beta = 83.87(3)^\circ$, $\gamma = 78.18(4)^\circ$, $V =$

$1808(2) \text{ \AA}^3$, $Z = 1$, $D_x = 1.465 \text{ g cm}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71073 \text{ \AA}$, $\mu = 9.35 \text{ cm}^{-1}$, $F(000) = 822$, $T = 295 \text{ K}$, $R = 0.069$ for 3204 unique reflections with $F_o^2 > 3\sigma(F_o^2)$. The unit cell consists of an edge-sharing bitetrahedral $[\text{Co}_2\text{Cl}_6]^{2-}$ dimer with two (crystallographically related) methylated phosphine counterions, CH_3TMPP^+ , and two interstitial solvent

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molecules (dichloromethane). The average Co—Cl distances are 2.342 (2) Å for the bridging chlorides Cl(3) and Cl(3') and 2.221 (2) Å for the terminal chlorides Cl(1) and Cl(2). The non-bonding Co...Co distance is 3.245 (2) Å.

Introduction. One of our current research projects focuses on the coordination chemistry of the triphenylphosphine derivative tris(2,4,6-trimethoxyphenyl)phosphine (TMPP). Our interest in TMPP compounds revolves around their high reactivity with small molecules owing to the presence of one or more labile metal-ether interactions. This unusual ligand has exhibited various coordination modes: monodentate and bidentate (Dunbar & Haefner, 1991), chelating tridentate (Dunbar & Haefner, 1990; Dunbar, Haefner & Pence, 1989) and a combination of bridging and chelating tridentate (Chen & Dunbar, 1990). Recently, we reported the structure of [HTMPP]₃W₂Cl₉ (Dunbar & Pence, 1991), in which three protonated phosphines serve as cations in a salt of the multiply bonded anion [W₂Cl₉]³⁻.

As part of an attempt to crystallize the adduct CoCl₂(TMPP), we isolated the title compound in which two methylated phosphines serve as counterions in a salt of [Co₂Cl₆]²⁻.

Experimental. Anhydrous CoCl₂ (0.112 g, 0.94 mmol) was reacted with one equivalent of TMPP (0.500 g, 0.94 mmol) in 10 ml of freshly distilled, deoxygenated benzene. The reaction mixture was stirred at room temperature for five days during which time a bright blue solid formed. This was collected by filtration and washed with copious amounts of benzene. The crude product was recrystallized from a dichloromethane solution which was layered with toluene. Blue crystals formed within 24 h at room temperature.

A crystal of approximate dimensions 0.60 × 0.35 × 0.20 mm was selected and mounted in a glass capillary which was then sealed with epoxy cement. The crystal was examined on a Nicolet P3 diffractometer using graphite-monochromated Mo K α radiation. Cell parameters were refined from a least squares determination of 19 reflections with $20 < 2\theta < 25^\circ$. Intensity data were collected at room temperature by using a θ - 2θ scan mode from 4–40° in 2θ . $0 \leq h \leq 10$, $-12 \leq k \leq 12$, $-12 \leq l \leq 12$. Three intensity standards were monitored at regular intervals and showed no significant decay. An absorption correction using DIFABS (Walker & Stuart, 1983) was applied.

The position of the Co atom was found by direct methods (SHELXS86; Sheldrick, 1986). The remaining non-H atoms were found through successive difference maps and least-squares cycles by using scattering factors and programs from the Enraf-

Nonius (1979) *Structure Determination Package*. All atoms were refined with anisotropic thermal factors with the exception of a C and a Cl atom of methylene chloride which were refined with isotropic thermal parameters. The positions of the H atoms were calculated and then refined with fixed thermal parameters. In the final cycle, 396 parameters were refined using 3204 unique reflections ($R_{int} = 1.4\%$) with $F_o^2 > 3\sigma(F_o^2)$. The structure refinement converged with $R = 0.069$ and $wR = 0.090$, $w = 4F_o^2[\sigma^2(I) + (0.05F_o^2)^2]^{-1}$, and a goodness of fit of 2.538. The ratio of max. shift to e.s.d. was 0.02. The highest positive peak from the final difference map was 1.73 e \AA^{-3} and was associated with the methylene chloride. The methylene chloride molecule is disordered but attempts to model the disorder in a chemically sensible manner proved unsatisfactory. The largest negative peak was 1.08 e \AA^{-3} . All calculations were performed on a VAXSTATION 2000 computer.

Discussion. The refined atomic coordinates and equivalent isotropic parameters are presented in Table 1* and selected bond distances and angles are listed in Table 2. Fig. 1 depicts the molecular structures of the two ions. As Fig. 1 clearly shows, the dicobalt anion consists of two edge-sharing tetrahedra, with two terminal and two bridging chlorides per metal atom. The methyl phosphonium cation exhibits the characteristic propeller arrangement found in aromatic tertiary phosphines.

The existence of the [Co₂Cl₆]²⁻ ion has been documented in the decomposition reactions of CoCl₂ adducts and in the chemistry of the mononuclear complex [CoCl₄]²⁻ with the chloride salts Et₄NCl, NH₄Cl or MCl ($M = \text{Li, K}$) (Desai, 1954; Kazi, 1956; Makarov, Malyshev & Izotov, 1968; Bobbitt & Gladden, 1972; Bondarevski, Izotov & Kopytov, 1973; Paul, Sharma & Verma, 1974, 1976). To our knowledge only two salts of [Co₂Cl₆]²⁻ have been previously structurally characterized: these are [CoClN₆P₆(NMe₂)₁₂]₂[Co₂Cl₆].2CHCl₃ (Harrison & Trotter, 1973) and [Co₂(C₅Me₅)(μ -Cl)₃]₂[Co₂Cl₆] (Olson & Dahl, 1986).

In (1), the average Co—Cl (bridge) distance is intermediate between those of the two previous structures found in the literature (2.336 and 2.378 Å). The Co—Cl—Co and the Cl—Co—Cl bond angles are more distorted from ideal geometry than the previous two examples (89.1 and 90.2, 90.1

* Lists of structure factors, anisotropic thermal parameters, full bond lengths and angles including those involving H atoms, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54086 (41 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic positional parameters and equivalent isotropic displacement parameters (\AA^2) and their e.s.d.'s for (1)

$$B_{\text{eq}} = (1/3) \sum_i \sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	B_{eq}
Co(1)	0.3618 (1)	-0.92560 (9)	-0.53779 (9)	4.40 (3)
Cl(1)	0.2884 (2)	-0.8800 (2)	-0.6970 (2)	5.92 (7)
Cl(2)	0.2306 (3)	-0.8543 (3)	-0.4429 (2)	9.06 (9)
Cl(3)	0.4396 (2)	-1.1188 (2)	-0.4544 (2)	4.91 (6)
P(1)	0.2831 (2)	-0.2919 (1)	-0.8806 (1)	2.82 (5)
C(28)	0.1863 (8)	-0.3438 (6)	-0.9384 (6)	3.9 (2)
C(1)	0.2285 (7)	-0.1434 (5)	-0.9452 (5)	2.7 (2)
C(2)	0.1599 (7)	-0.0792 (6)	-0.8941 (5)	3.0 (2)
C(3)	0.1203 (7)	0.0348 (6)	-0.9497 (6)	3.6 (2)
C(4)	0.1466 (7)	0.0875 (6)	-1.0583 (6)	3.5 (2)
C(5)	0.2082 (7)	0.0278 (6)	-1.1131 (6)	3.3 (2)
C(6)	0.2454 (7)	-0.0868 (6)	-1.0556 (5)	3.3 (2)
O(1)	0.1328 (5)	-0.1370 (4)	-0.7883 (4)	4.2 (1)
O(2)	0.1055 (6)	0.2001 (4)	-1.1049 (5)	4.9 (2)
O(3)	0.3038 (5)	-0.1531 (4)	-1.1021 (4)	4.0 (1)
C(7)	0.081 (1)	-0.0756 (7)	-0.7283 (6)	5.6 (3)
C(8)	0.135 (1)	0.2618 (7)	-1.2158 (8)	6.6 (3)
C(9)	0.336 (1)	-0.1032 (7)	-1.2135 (6)	5.0 (3)
C(10)	0.4455 (7)	-0.3310 (5)	-0.9117 (5)	2.8 (2)
C(11)	0.5320 (7)	-0.2599 (5)	-0.9622 (2)	2.9 (2)
C(12)	0.6537 (7)	-0.2982 (6)	-0.9868 (6)	3.6 (2)
C(13)	0.6902 (7)	-0.4117 (6)	-0.9610 (6)	3.6 (2)
C(14)	0.6098 (8)	-0.4871 (6)	-0.9082 (6)	3.7 (2)
C(15)	0.4894 (8)	-0.4474 (6)	-0.8827 (5)	3.4 (2)
O(4)	0.4946 (5)	-0.1499 (4)	-0.9843 (4)	3.8 (1)
O(5)	0.8063 (5)	-0.4550 (4)	-0.9857 (4)	4.9 (2)
O(6)	0.4029 (5)	-0.5140 (4)	0.8296 (4)	4.2 (1)
C(16)	0.5622 (9)	-0.0708 (6)	-1.0661 (6)	4.6 (2)
C(17)	0.8844 (9)	-0.3780 (8)	-1.0564 (8)	6.2 (3)
C(18)	0.439 (1)	-0.6311 (6)	-0.7910 (8)	5.6 (3)
C(19)	0.2701 (7)	-0.3545 (5)	-0.7385 (5)	2.9 (2)
C(20)	0.2029 (7)	-0.4418 (6)	-0.6754 (5)	3.6 (2)
C(21)	0.2075 (9)	-0.4947 (7)	-0.5650 (6)	4.8 (2)
C(22)	0.2774 (9)	-0.4555 (7)	-0.5161 (6)	4.8 (2)
C(23)	0.3446 (8)	-0.3705 (7)	-0.5711 (6)	4.3 (2)
C(24)	0.3390 (7)	-0.3217 (6)	-0.6818 (5)	3.3 (2)
O(7)	0.1331 (5)	-0.4739 (4)	-0.7281 (4)	4.5 (1)
O(8)	0.2745 (7)	-0.5131 (6)	-0.4056 (4)	7.1 (2)
O(9)	0.4053 (5)	-0.2386 (4)	-0.7456 (4)	4.0 (1)
C(25)	0.069 (1)	-0.5669 (7)	-0.6699 (8)	6.7 (3)
C(26)	0.348 (1)	-0.4837 (9)	-0.3467 (7)	7.9 (3)
C(27)	0.482 (1)	-0.2008 (8)	-0.6983 (7)	6.9 (3)
C(29)	0.051 (1)	0.864 (1)	0.634 (1)	10.8 (4)*
Cl(4)	0.1016 (4)	0.7539 (4)	0.7660 (3)	13.3 (2)
Cl(5)	0.1207 (6)	0.7988 (5)	0.5536 (4)	15.8 (2)*

Table 2. Selected bond distances (\AA) and angles ($^\circ$) for the anion $[\text{Co}_2\text{Cl}_6]^{2-}$

Co(1)	Co(1')	3.245 (2)	Co(1)	Cl(3)	2.345 (2)		
Co(1)	Cl(1)	2.223 (2)	Co(1)	Cl(3')	2.339 (2)		
Co(1)	Cl(2)	2.218 (2)					
Cl(3)	Co(1)	Cl(3')	92.32 (6)	Cl(1)	Co(1)	Cl(3)	109.42 (7)
Co(1)	Cl(3)	Co(1')	87.68 (6)	Cl(2)	Co(1)	Cl(3)	116.99 (7)
Cl(1)	Co(1)	Cl(2)	113.08 (8)				

and 89.9°). Furthermore, the non-bonding $\text{Co}\cdots\text{Co}$ distance in the present structure is shorter than the corresponding distances in the other two complexes by 0.03 and 0.12 \AA . The considerable distortion from ideal tetrahedral geometry in the present case is obviously a result of packing influences.

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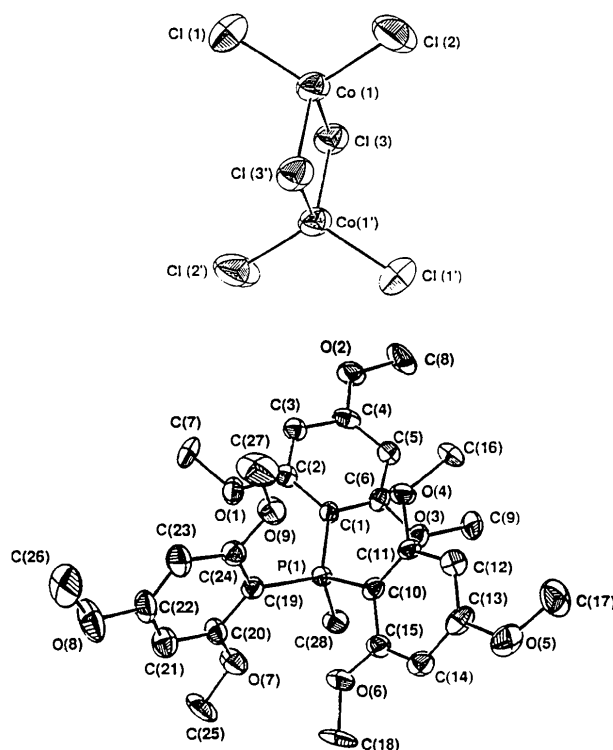


Fig. 1. ORTEP (Johnson, 1976) plots of the two independent ions contained in the unit cell of (1). Atoms are represented by thermal ellipsoids drawn at the 50% probability level.

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