The potassium ion is coordinated in a very distorted octahedron by four O atoms and two chloride ions. Fig. 2 shows the alternating layers of cations (K^+) and complex anions parallel to the diagonal (101).

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Structure of Tetraethylammonium Nonacarbonyl-μ_3-{[dichloro(undecacarbonylcobaltio)silyl]oxymethylidyne}-tricobaltate, $[Et_4N][Cl_2SiCo_7(CO)_{21}]$

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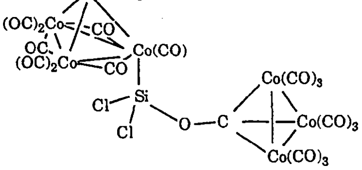
Abstract. $C_{29}H_{20}Cl_2Co_7NO_{21}Si$, $M_r = 1230.0$, monoclinic, $P2_1/c$, $a = 9.110\,(4)$, $b = 22.472\,(9)$, $c = 21.01\,(1)$ Å, $\beta = 95.28\,(4)°$, $V = 4283\,(3)$ Å^3, $Z = 4$, $D_x = 1.91$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 29$ cm^{-1}, $F(000) = 2424$, $T = 148$ K, $R = 0.0555$ for 2626 $[I > 3\sigma(I)]$ reflections. The Si atom is bonded to two Cl atoms [Si—Cl (av.) = 2.094 (6) Å, Cl—Si—Cl = 101.7 (2)°], to a $Co_4(CO)_{11}$ moiety [Si—Co = 2.209 (5) Å, Co—Si—Cl (av.) = 118.0 (3)°], and to the O atom of a μ_3-CO group which bridges a $Co_3(CO)_9$ unit [Si—O = 1.67 (1), O—C = 1.32 (2) Å, O—Si—Cl(av.) = 102.9 (4), O—Si—Co = 111.1 (4)°].

Introduction. The reaction of $Si[Co_2(CO)_7]_2$ with $[Et_4N][Co(CO)_4]$ proceeds to give the mixed salt $[Et_4N]_3[SiCo_9(CO)_{21}][Co(CO)_4]$ in high yields (Mackay, Nicholson & Sims, 1984; Barris, 1986). On further investigation of this reaction, $[Et_4N][Cl_2Si\text{-}Co_7(CO)_{21}]$ (I) has now been isolated as a minor component of the product mixture by extraction into diethyl ether, and has been characterized by X-ray crystallography. The Cl atoms in $[Et_4N][Cl_2SiCo_7(CO)_{21}]$ appear to be derived from residual $[Et_4N]Cl$ carried over from the preparation of the $[Et_4N][Co(CO)_4]$ reagent.



(I)

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Experimental. The infrared spectrum of $[Et_4N][Cl_2SiCo_7(CO)_{21}]$ in CH_2Cl_2 exhibits seven peaks in the carbonyl stretching region (2099*vw*, 2070*w*, 2048*vs*, 2026*s*, 2004*m*, 1865*vw*, 1824*w* cm^{-1}). The two weak peaks at 1865 and 1824 cm^{-1} represent bridging-carbonyl stretching modes, and the remaining five are terminal-carbonyl modes.

Rectangular black plate-like crystals of $[Et_4N][Cl_2SiCo_7(CO)_{21}]$ were grown by slow diffusion of hexane into a diethyl ether solution at 277 K. Preliminary precession photography, using a selected crystal of dimensions 0.76 × 0.34 × 0.02 mm, established monoclinic symmetry and showed systematic absences uniquely defining space group $P2_1/c$. Intensity data were collected using a Nicolet *P*3 automated diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Lattice parameters were obtained from 22 automatically centered reflections ($13 < 2\theta < 30°$). 5251 unique reflections, $4 < 2\theta < 45°$, were collected using ω–2θ scans. Standard reflections were monitored regularly and showed no significant variation. 2626 data with $I > 3\sigma(I)$ were corrected for Lorentz and polarization effects. An empirical absorption correction was applied, based on a series of φ scans, with transmission factors between 0.942 and 0.555. Coordinates for the Si and seven Co atoms were obtained by direct methods and the structure was developed routinely. With Co, Si and Cl atoms anisotropic, other non-H atoms isotropic and with H atoms in calculated positions (309 parameters), successive full-matrix least-squares refinements based on F^2 converged with $R = 0.0555$, $wR = 0.0511$ and $w = [\sigma^2(F) + 0.000573F^2]^{-1}$, maximum $\Delta/\sigma = 0.09$. The final difference map showed no features greater than $0.75/-0.60$ e $Å^{-3}$. Atomic scattering factors and f' and f'' values were obtained from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were performed with *SHELX* programs (Sheldrick, 1976, 1986). Atomic positional parameters are listed in Table 1 and selected bond lengths and angles are given in Table 2.*

Table 1. *Final positional and thermal parameters* ($Å^2$) *for the title compound*

Co, Si and Cl atoms were refined with anisotropic thermal parameters; U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. O, C and N atoms were refined with isotropic thermal parameters.

	x	y	z	U_{eq}/U_{iso}
Co(1)	0.3405 (2)	0.6032 (1)	0.3949 (1)	0.016
Co(2)	0.1140 (2)	0.5389 (1)	0.3958 (1)	0.018
Co(3)	0.0855 (2)	0.6470 (1)	0.3786 (1)	0.020
Co(4)	0.1719 (2)	0.5847 (1)	0.2943 (1)	0.016
Co(5)	−0.1189 (2)	0.7359 (1)	0.0955 (1)	0.023
Co(6)	−0.3149 (2)	0.6593 (1)	0.0924 (1)	0.020
Co(7)	−0.0915 (2)	0.6428 (1)	0.0346 (1)	0.024
Si(1)	−0.0160 (5)	0.5747 (2)	0.2208 (2)	0.019
Cl(1)	−0.2277 (4)	0.5613 (2)	0.2489 (2)	0.024
Cl(2)	−0.0006 (4)	0.5059 (2)	0.1542 (2)	0.028
O(1)	−0.037 (1)	0.6351 (4)	0.1751 (5)	0.019 (3)
O(11)	0.426 (1)	0.6142 (5)	0.5325 (6)	0.041 (3)
O(12)	0.533 (1)	0.5078 (5)	0.3539 (5)	0.028 (3)
O(13)	0.481 (1)	0.7106 (5)	0.3504 (6)	0.034 (3)
O(21)	0.283 (1)	0.4621 (5)	0.4873 (6)	0.036 (3)
O(22)	−0.165 (1)	0.4736 (5)	0.3893 (6)	0.038 (3)
O(23)	0.038 (1)	0.6074 (5)	0.5073 (6)	0.036 (3)
O(24)	0.200 (1)	0.4545 (4)	0.2986 (5)	0.025 (3)
O(31)	0.181 (1)	0.7550 (5)	0.4445 (6)	0.036 (3)
O(32)	−0.225 (2)	0.6774 (6)	0.3448 (7)	0.059 (4)
O(34)	0.169 (1)	0.7123 (5)	0.2640 (5)	0.029 (3)
O(41)	0.374 (1)	0.5723 (5)	0.1966 (6)	0.036 (3)
O(51)	−0.263 (1)	0.8207 (5)	−0.0004 (6)	0.050 (4)
O(52)	−0.173 (1)	0.7854 (5)	0.2201 (6)	0.049 (4)
O(53)	0.195 (1)	0.7657 (5)	0.1007 (6)	0.043 (3)
O(61)	−0.502 (1)	0.7160 (6)	−0.0135 (7)	0.050 (4)
O(62)	−0.428 (1)	0.5377 (5)	0.0883 (6)	0.041 (3)
O(63)	−0.453 (1)	0.6957 (5)	0.2072 (6)	0.040 (3)
O(71)	−0.156 (1)	0.7037 (6)	−0.0902 (7)	0.058 (4)
O(72)	−0.171 (1)	0.5213 (5)	−0.0034 (6)	0.041 (3)
O(73)	0.227 (1)	0.6239 (5)	0.0568 (6)	0.046 (3)
C(1)	−0.114 (2)	0.6542 (7)	0.1227 (8)	0.021 (4)
C(11)	0.390 (2)	0.6104 (7)	0.4793 (8)	0.022 (4)
C(12)	0.460 (2)	0.5454 (7)	0.3708 (7)	0.018 (4)
C(13)	0.427 (2)	0.6687 (7)	0.3675 (8)	0.021 (4)
C(21)	0.217 (2)	0.4932 (7)	0.4497 (9)	0.029 (4)
C(22)	−0.055 (2)	0.5007 (7)	0.3916 (8)	0.029 (4)
C(23)	0.065 (2)	0.6018 (7)	0.4531 (8)	0.020 (4)
C(24)	0.175 (2)	0.5031 (7)	0.3165 (7)	0.017 (4)
C(31)	0.141 (2)	0.7130 (7)	0.4188 (7)	0.018 (4)
C(32)	−0.102 (2)	0.6631 (8)	0.3606 (9)	0.037 (5)
C(34)	0.152 (2)	0.6686 (7)	0.2936 (8)	0.020 (4)
C(41)	0.295 (2)	0.5781 (7)	0.2344 (8)	0.025 (4)
C(51)	−0.204 (2)	0.7884 (8)	0.0382 (9)	0.033 (5)
C(52)	−0.151 (2)	0.7679 (7)	0.1696 (8)	0.020 (4)
C(53)	0.072 (2)	0.7551 (7)	0.0975 (8)	0.033 (5)
C(61)	−0.430 (2)	0.6933 (8)	0.0279 (9)	0.038 (5)
C(62)	−0.384 (2)	0.5841 (8)	0.0911 (8)	0.028 (4)
C(63)	−0.399 (2)	0.6820 (7)	0.1627 (9)	0.029 (4)
C(71)	−0.133 (2)	0.6789 (7)	−0.0417 (9)	0.029 (4)
C(72)	−0.139 (2)	0.5694 (8)	0.0122 (9)	0.032 (5)
C(73)	0.100 (2)	0.6320 (7)	0.0461 (9)	0.037 (5)
N(1)	0.395 (1)	0.8772 (5)	0.2859 (6)	0.021 (3)
C(81)	0.509 (2)	0.9266 (6)	0.2981 (8)	0.023 (4)
C(82)	0.653 (2)	0.9069 (8)	0.3332 (9)	0.042 (5)
C(83)	0.364 (2)	0.8476 (8)	0.3494 (8)	0.036 (5)
C(84)	0.308 (2)	0.8897 (8)	0.3968 (9)	0.046 (5)
C(85)	0.257 (2)	0.9057 (7)	0.2547 (8)	0.034 (5)
C(86)	0.127 (2)	0.8661 (8)	0.2394 (9)	0.042 (5)
C(87)	0.450 (2)	0.8285 (6)	0.2443 (7)	0.021 (4)
C(88)	0.481 (2)	0.8500 (8)	0.1791 (8)	0.040 (5)

Discussion. The structure comprises discrete Et_4N^+ cations and $[Cl_2SiCo_7(CO)_{21}]^-$ anions. The geometry of the anion is illustrated in Fig. 1 and consists of $Co_4(CO)_{11}$ and $OCCo_3(CO)_9$ cluster units linked through an $SiCl_2$ group. Bonding about the Si atom is essentially tetrahedral, although the bulk of the $Co_4(CO)_{11}$ group causes some distortion. The mean Si—Cl bond length (2.094 Å) approximates to the sum of the covalent radii of Si and Cl. The Si—Co bond, however, is surprisingly short [2.209 (5) Å]. This compares with Si—Co bond lengths of 2.249 (8) and 2.254 (3) Å in $(CO)_4CoSi(Cl)_2OCCo_3(CO)_9$ (van Teil, 1991) and $(CO)_4CoSiCl_3$ (Robinson & Ibers, 1967) respectively. In each of the last two examples the Si—Co bond is *trans* to a CO ligand, whereas in the title compound it is opposite to a Co—Co bond. These bond lengths therefore fall into the pattern

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* Lists of structure factors, full bond parameters, anisotropic thermal parameters, and calculated H-atom positions have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54861 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI0098]

Table 2. *Selected bond lengths* (Å) *and angles* (°) *for the title compound*

Co(1)—Co(2)	2.521 (3)	Co(4)—Si(1)	2.209 (5)
Co(1)—Co(3)	2.517 (3)	Si(1)—Cl(1)	2.089 (6)
Co(1)—Co(4)	2.530 (3)	Si(1)—Cl(2)	2.100 (7)
Co(2)—Co(3)	2.466 (3)	Si(1)—O(1)	1.67 (1)
Co(2)—Co(4)	2.469 (3)	O(1)—C(1)	1.32 (2)
Co(3)—Co(4)	2.444 (3)	Co(5)—C(1)	1.92 (2)
Co(5)—Co(6)	2.477 (3)	Co(6)—C(1)	1.89 (2)
Co(5)—Co(7)	2.478 (3)	Co(7)—C(1)	1.90 (2)
Co(6)—Co(7)	2.493 (3)		

Co(2)—Co(1)—Co(3)	58.6 (1)	Co(5)—Co(6)—C(1)	50.1 (5)
Co(2)—Co(1)—Co(4)	58.5 (1)	Co(7)—Co(6)—C(1)	49.0 (5)
Co(3)—Co(1)—Co(4)	57.9 (1)	Co(5)—Co(7)—Co(6)	59.8 (1)
Co(1)—Co(2)—Co(3)	60.6 (1)	Co(5)—Co(7)—C(1)	50.0 (5)
Co(1)—Co(2)—Co(4)	60.9 (1)	Co(6)—Co(7)—C(1)	48.6 (4)
Co(3)—Co(2)—Co(4)	59.4 (1)	Co(4)—Si(1)—Cl(1)	119.6 (3)
Co(1)—Co(3)—Co(2)	60.8 (1)	Co(4)—Si(1)—Cl(2)	116.5 (2)
Co(1)—Co(3)—Co(4)	61.3 (1)	Co(4)—Si(1)—O(1)	111.1 (4)
Co(2)—Co(3)—Co(4)	60.4 (1)	Cl(1)—Si(1)—Cl(2)	101.7 (2)
Co(1)—Co(4)—Co(2)	60.6 (1)	Cl(1)—Si(1)—O(1)	102.8 (4)
Co(1)—Co(4)—Co(3)	60.8 (1)	Cl(2)—Si(1)—O(1)	103.1 (4)
Co(1)—Co(4)—Si(1)	166.5 (2)	Si(1)—O(1)—C(1)	140 (1)
Co(2)—Co(4)—Co(3)	60.3 (1)	Co(5)—C(1)—Co(6)	81.1 (6)
Co(2)—Co(4)—Si(1)	110.4 (2)	Co(5)—C(1)—Co(7)	80.8 (6)
Co(3)—Co(4)—Si(1)	106.5 (2)	Co(5)—C(1)—O(1)	124 (1)
Co(6)—Co(5)—Co(7)	60.4 (1)	Co(6)—C(1)—Co(7)	82.3 (6)
Co(6)—Co(5)—C(1)	48.8 (5)	Co(6)—C(1)—O(1)	137 (1)
Co(7)—Co(5)—C(1)	49.2 (5)	Co(7)—C(1)—O(1)	132 (1)
Co(5)—Co(6)—Co(7)	59.8 (1)		

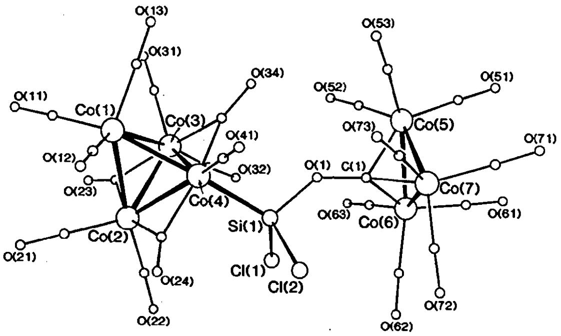

Fig. 1. A perspective view of the anion [Cl$_2$SiCo$_7$(CO)$_{21}$]$^-$.

that CO groups exhibit a strong *trans* influence on metal–metal bonds involving Group 14 elements, as discussed elsewhere (Curnow, Nicholson & Severinsen, 1990).

The —Co$_4$(CO)$_{11}$ portion of the [Cl$_2$SiCo$_7$(CO)$_{21}$]$^-$ cluster adopts the C_{3v} configuration of Co$_4$(CO)$_{12}$ where three μ_2-CO groups bridge the edges of a Co$_3$ triangle which is capped by an apical Co with all-terminal carbonyls. The Co$_{\text{basal}}$—Co$_{\text{basal}}$ [2.459 (3) Å] and Co$_{\text{basal}}$—Co$_{\text{apical}}$ [2.522 (3) Å] bonds are comparable with the appropriate bonds in related compounds {Co$_4$(CO)$_{11}$PR_3, where R = Ph, Me (Darensbourg & Incorvia, 1981; Bartl, Boese & Schmid, 1981); [Co$_4$(CO)$_{11}Y$]$^-$, where Y = COMe, COOMe (Went, Brock & Schriver, 1986; Horwitz & Shriver, 1984); and [Co$_4$(CO)$_{11}$GeCo$_3$(CO)$_9$]$^-$ (Duffy, Mackay, Nicholson & Thomson, 1982)}, and the overall mean Co—Co length within the tetrahedron [2.489 (3) Å] is almost identical to that in Co$_4$(CO)$_{12}$ [2.49 Å (Wei, 1969)]. The —Si(Cl)$_2$-OCCo$_3$(CO)$_9$ group is coordinated to one of the basal Co atoms, Co(4), in an axial position. The longest Co—Co bond [2.530 (3) Å] is that located *trans* to the Si—Co bond. The presence of the —Si(Cl)$_2$OCCo$_3$(CO)$_9$ substituent also induces significant asymmetry in the two carbonyls which bridge to the Si-bonded Co atom. These two bridging carbonyls are displaced toward the substituted metal centre [C—Co$_{\text{unsubst.}}$ (av.) = 1.99 (2), C—Co$_{\text{subst.}}$ (av.) = 1.89 (2) Å], while the third bridging carbonyl is more symmetric.

Most monosubstituted derivatives of Co$_4$(CO)$_{12}$, for which structures have been reported, adopt this same configuration with substitution occurring at the axial position on a basal Co. The basal Co atoms are bonded to a greater number of carbonyl ligands, which permits better charge dispersion for strong σ-donating substituents. [Co$_4$(CO)$_{11}$I]$^-$ (Albano, Bragga, Longoni, Campanella, Ceriotti & Chini, 1980), with a more electronegative substituent, I, is the one exception. Here the I atom is attached to the apical Co, although a small amount of the basal isomer was detected in the crystal.

The three Co atoms in the —OCCo$_3$(CO)$_9$ moiety form an equilateral triangle. The interatomic distances and angles of the —OCCo$_3$(CO)$_9$ moiety are comparable with those found in other oxymethylidyne clusters of this type, *e.g.* Et$_3$NB(H)$_2$OCCo$_3$(CO)$_9$ (Klanberg, Askew & Guggenberger, 1968), Et$_3$NB(Cl)$_2$OCCo$_3$(CO)$_9$ (Batzel, Muller & Allmann, 1975), Cp$_2$Ti(Cl)OCCo$_3$(CO)$_9$ (Schmid, Batzel & Stutte, 1976), Cp$_2$Cr$_2$(μ-OCMe$_3$)$_2$-[μ-OCCo$_3$(CO)$_9$] (Nefedov *et al.*, 1990), and (CO)$_4$CoSi(Cl)$_2$OCCo$_3$(CO)$_9$ (van Teil, 1991). The C(1)—O(1) and Si(1)—O(1) bonds are both relatively short [1.32 (2) and 1.67 (1) Å, respectively] which, together with the short Si—Co(4) bond, suggests some delocalized π bonding over the C—O—Si—Co link between the two cluster fragments. The Si(1)—O(1)—C(1) angle of 140 (1)° is also very large, probably owing to steric repulsion between the bulky groups at either end of the Si—O—C linkage. This angle seems to be very flexible with the equivalent angles in the other oxymethylidyne clusters listed above ranging from 132 to 154°.

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Structure of 1,6-Hexanediammonium Metavanadate

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Abstract. $[H_3N—(CH_2)_6—NH_3]^{2+}.(VO_3^-)_2$, $M_r = 316.10$, orthorhombic, $Pbca$, $a = 5.379\,(4)$, $b = 11.074\,(9)$, $c = 19.58\,(2)$ Å, $V = 1166\,(2)$ Å^3, $Z = 4$, $D_m = 1.76\,(1)$, $D_x = 1.800$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 15.65$ cm^{-1}, $F(000) = 648$, room temperature, final $R = 0.0339$ for 918 observed reflections. The structure is made up of infinite $(VO_3)_\infty$ chains running parallel to the a axis. The doubly protonated hexanediamine molecule is located on a centre of symmetry.

Introduction. Typical structures of anhydrous metavanadates M^IVO_3 comprise infinite chains of corner-sharing VO_4 tetrahedra. Fourfold O-atom coordination of V atoms was found by Synecek & Hanic (1954) in NH_4VO_3, Petrášová, Madar & Hanic (1958) in KVO_3, Shannon & Calvo (1973) in $LiVO_3$, Marumo, Isobe & Iwai (1974) in α-$NaVO_3$, and Ganne, Piffard & Tournoux (1974) in $TlVO_3$.

In the $M^{II}(VO_3)_2$ metavanadate structures there is greater variability among the VO_n coordination polyhedra. Most of the previously investigated metavanadates have a distorted octahedral coordination around the V atoms characterized by five strong and one weak (~2.6 Å) V—O interactions. Examples are β-$Cd(VO_3)_2$ (Bouloux & Galy, 1969), $Mg(VO_3)_2$ (Ng & Calvo, 1972), $Co(VO_3)_2$ (Sauerbrei, 1972), $Zn(VO_3)_2$ (Angenault & Rimsky, 1968; Andreetti, Calestani, Montenero & Bettinelli, 1984), $Cu(VO_3)_2$ (Calvo & Manolescu, 1973), $Pb(VO_3)_2$ (I) (Jordan & Calvo, 1974) and β-$Hg(VO_3)_2$ (Angenault, 1970).

Loss of the sixth weak interaction is characteristic for the structure $Pb(VO_3)_2$ (II) (Calestani, Andreetti, Montenero & Bettinelli, 1985), which consists of columns of double chains of edge-sharing VO_5 square pyramids. This coordination was found in the structure $Co(VO_3)_2$ (Jasper-Tönnies & Müller-Buschbaum, 1984). In the structures $Ca(VO_3)_2$ and α-$Cd(VO_3)_2$ (Bouloux, Perez & Galy, 1972) and α-$Sr(VO_3)_2$ (Karpov, Simonov, Krasnenko & Zabara, 1989) are found trigonal bipyramidal coordinations of the atom V^V.

The structures of $Pb(VO_3)_3$ (III) (Calestani, Andreetti, Montenero, Bettinelli & Rebizant, 1985) and $Ba(VO_3)_2$ (Launay & Thoret, 1973) are different from those of other $M^{II}(VO_3)_2$ systems and consist of chains of corner-sharing VO_4 tetrahedra. The structure of $[H_3N—(CH_2)_6—NH_3]^{2+}.(VO_3^-)_2$ has been investigated to provide further structural data on the metavanadates.

Experimental. 1,6-Hexanediammonium metavanadate was prepared by dissolving V_2O_5 in aqueous solution of hexanediamine with gentle heating. The colourless solution was slowly cooled at room temperature and then filtrated. For preparation of crys-

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