

## Synthesis and Structure of a Complex $\text{Co}_6(\text{C}_5\text{Me}_5)_4\text{Cl}_{12}$ Salt Containing Confacial Bioctahedral $[\text{Co}_2(\eta^5\text{-C}_5\text{Me}_5)_2(\mu_2\text{-Cl})_3]^+$ Monocations and Edge-Shared Bitetrahedral $[\text{Co}_2\text{Cl}_4(\mu_2\text{-Cl})_2]^{2-}$ Dianions

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**Abstract.** Bis[tri- $\mu$ -chloro-bis( $\eta^5$ -pentamethylcyclopentadienyl)dicobalt(III)] di- $\mu$ -chloro-bis[dichlorocobaltate(II)],  $[\text{Co}_2\text{Cl}_3(\text{C}_{10}\text{H}_{15})_2]_2^+[\text{Co}_2\text{Cl}_6]^{2-}$ ,  $M_r = 1319.8$ , triclinic,  $P\bar{1}$ ,  $a = 14.398$  (5),  $b = 14.278$  (8),  $c = 9.393$  (3) Å,  $\alpha = 109.19$  (3),  $\beta = 129.99$  (2),  $\gamma = 87.25$  (4)°,  $V = 1361$  (1) Å<sup>3</sup>,  $Z = 1$ ,  $D_x = 1.61$  g cm<sup>-3</sup>,  $\text{Mo } K\alpha$ ,  $\lambda = 0.71073$  Å,  $\mu = 24.1$  cm<sup>-1</sup>,  $F(000) = 666$ ,  $T = 295$  K,  $R_1(F) = 0.062$  for 2105 observed reflections. The title salt was unexpectedly isolated from the reaction of the  $[\text{Co}_2(\eta^5\text{-C}_5\text{Me}_5)_2(\mu_2\text{-CO})_2]^-$  monoanion with  $\text{GeMe}_2\text{Cl}_2$ . The  $[\text{Co}_2(\eta^5\text{-C}_5\text{Me}_5)_2(\mu_2\text{-Cl})_3]^+$  monocation of 1 ( $C_1$ ) site symmetry consists of two eclipsed  $\text{Co}(\eta^5\text{-C}_5\text{Me}_5)$  fragments linked by three bridging chlorine atoms. The resulting face-shared bioctahedral geometry with a nonbonding  $\text{Co}\cdots\text{Co}$  distance of 2.914 (2) Å between the two  $d^6$   $\text{Co}^{\text{III}}$  atoms ideally has  $mm2$  ( $C_{2v}$ ) symmetry; the assumption of cylindrical symmetry for each pentamethylcyclopentadienyl ring gives rise to a pseudo  $\bar{6}2m$  ( $D_{3h}$ ) geometry. The uncommon  $[\text{Co}_2\text{Cl}_4(\mu_2\text{-Cl})_2]^{2-}$  dianion of  $\bar{1}$  ( $C_i$ ) site symmetry ideally conforms to an edge-shared bitetrahedral geometry of  $mmm$  ( $D_{2h}$ ) symmetry with a nonbonding distance of 3.366 (3) Å between the two  $d^7$   $\text{Co}^{\text{II}}$  atoms.

**Introduction.** As part of our continuing investigation of the chemical reactivity of the metal–metal multiple-bonded  $[\text{Co}_2(\eta^5\text{-C}_5\text{Me}_5)_2(\mu_2\text{-CO})_2]^n$  series ( $n = 0, 1$ ) (Cirjak, Ginsburg & Dahl, 1982) with a variety of organometallic reagents (Cirjak, Huang, Zhu & Dahl, 1980), an attempt was made to prepare the unknown metal–metal single-bonded complex  $\text{Co}_2(\eta^5\text{-C}_5\text{Me}_5)_2(\text{CO})_2(\mu_2\text{-GeR}_2)$  by the addition of a two-electron-donating  $\text{GeMe}_2$  fragment across the double bond of the above-mentioned neutral inorganic ethylene analogue. The previously unreported metal–metal single-bonded  $\text{Co}_2(\eta^5\text{-C}_5\text{Me}_5)_2(\mu_2\text{-GeMe}_2)_3$  was also viewed as another likely product, especially because the electronically equivalent and structurally proven  $\text{Fe}_2(\text{CO})_6(\mu_2\text{-GeMe}_2)_3$  (Elder & Hall, 1969) with three bridging dimethylgermanium ligands had been synthesized (Brooks, Elder, Graham & Hall, 1968). The designed synthetic route to these dimethylgermanium-

bridged dicobalt complexes involving the reaction of  $\text{GeMe}_2\text{Cl}_2$  with  $\text{Na}^+[\text{Co}_2(\eta^5\text{-C}_5\text{Me}_5)_2(\mu_2\text{-CO})_2]^-$  is similar to that utilized (Theopold & Bergman, 1983) to prepare the crystallographically characterized methylene-bridged *trans*- $\text{Co}_2(\eta^5\text{-C}_5\text{H}_4\text{Me})_2(\text{CO})_2(\mu_2\text{-CH}_2)$  by reaction of  $\text{CH}_2\text{I}_2$  with  $\text{Na}^+[\text{Co}_2(\eta^5\text{-C}_5\text{H}_4\text{Me})_2(\mu_2\text{-CO})_2]^-$ . Our reaction led instead to the unexpected isolation of  $[\text{Co}_2(\eta^5\text{-C}_5\text{Me}_5)_2(\mu_2\text{-Cl})_3]_2^+[\text{Co}_2\text{Cl}_4(\mu_2\text{-Cl})_2]^{2-}$  (I) described herein.

**Experimental.** (I) was prepared under an inert atmosphere by the reaction of  $\text{Na}^+[\text{Co}_2(\eta^5\text{-C}_5\text{Me}_5)_2(\mu_2\text{-CO})_2]^-$  with a slowly added twofold excess of  $\text{GeMe}_2\text{Cl}_2$  in tetrahydrofuran at room temperature. After thirty minutes, the solvent was removed under vacuum and the residue washed with hexane to remove all neutral products. Extraction of the hexane-insoluble residue with dichloromethane gave a turquoise-blue solution which was filtered and slowly evaporated to yield suitable crystals (~5% yield) for X-ray diffraction analysis. Light-blue needle-shaped crystal (0.20 × 0.20 × 0.40 mm) mounted under argon inside Lindemann-glass capillary, which was then hermetically sealed.

X-ray data with graphite-monochromatized  $\text{Mo } K\alpha$  radiation, Syntex (Nicolet)  $P\bar{1}$  diffractometer;  $\theta$ – $2\theta$  scans, variable  $2\theta$  scan speeds (4.0–24.0° min<sup>-1</sup>); lattice parameters from 15 reflections within  $2\theta$  range 15–25°. Details of crystal alignment and data-collection parameters with listing of programs utilized (in addition to those specifically mentioned herein) given elsewhere (Byers & Dahl, 1980). 2681 data ( $0 \leq h \leq 14$ ;  $-14 \leq k \leq 14$ ;  $-7 \leq l \leq 7$ ) with  $3.0 \leq 2\theta \leq 40.0^\circ$ ; 2% max. intensity variation of two standard reflections monitored every 50 observations; empirical absorption correction based on  $\psi$  scans; 2105 independent reflections with  $I \geq 2.5\sigma(I)$ . Chosen triclinic cell is related to standard reduced triclinic cell (with  $a' = 9.393$ ,  $b' = 11.032$ ,  $c' = 14.278$  Å,  $\alpha' = 77.45$ ,  $\beta' = 70.81$ ,  $\gamma' = 89.27^\circ$ ) by transformation matrix (0,0,-1; -1,0,-1; 0,1,0). Structure determined by *MULTAN* (Germain, Main & Woolfson, 1971; Main, Lessinger, Woolfson, Germain & Declercq, 1977) and refined by full-matrix

least squares [ $\sum w_i(\Delta F)^2$  minimized] with *RAELS* (Rae, 1976); Co and Cl atoms anisotropic, and two  $\text{C}_5\text{Me}_5$  rings (including H atoms) each treated as rigid  $5mm$  ( $C_{5v}$ ) group (involving one variable ring C—C and one variable C—CH<sub>3</sub> distance) with thermal motion (Schomaker & Trueblood, 1968) described by a *TLX* model (Rae, 1975). Idealized tetrahedral hydrogen positions calculated (Calabrese, 1971) for each methyl substituent with fixed isotropic temperature factors. Refinement of this 132-parameter model converged at  $R_1(F) = 6.2\%$ ,  $wR(F) = 8.5\%$  [ $w_i = 1/\sigma^2(F_o)$ ]; final max. shift-to-e.s.d. ratio in last cycle 0.15. Goodness of fit 2.16. Final difference map revealed no unusual features with max. and min. heights 1.8 and  $-1.9\text{ e}\text{\AA}^{-3}$ . Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974).

**Discussion.** Table 1 gives the atomic positional parameters and equivalent isotropic thermal parameters.\* Interatomic distances and bond angles are presented in Table 2.

\* Lists of structure amplitudes, anisotropic thermal parameters, H-atom coordinates and selected least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42585 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates for non-hydrogen atoms and equivalent isotropic temperature factors

$$U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	$U_{\text{eq}}(\text{\AA}^2)$
Co(3)	0.86623 (14)	0.93800 (11)	0.2611 (2)	0.038
Co(1)	0.74736 (13)	0.49623 (11)	-0.0390 (2)	0.038
Co(2)	0.68690 (13)	0.27461 (11)	-0.1956 (2)	0.036
Cl(1)	0.9775 (3)	1.1114 (2)	0.4716 (5)	0.057
Cl(2)	0.8523 (3)	0.8780 (2)	-0.0031 (5)	0.058
Cl(3)	0.6852 (3)	0.9094 (3)	0.1829 (5)	0.080
Cl(4)	0.7189 (3)	0.3793 (2)	-0.3129 (4)	0.043
Cl(5)	0.8562 (3)	0.3888 (2)	0.1228 (4)	0.051
Cl(6)	0.5738 (3)	0.3882 (2)	-0.1653 (5)	0.051
C(1)	0.8477 (5)	0.6207 (4)	0.0081 (7)	0.045
C(2)	0.8894 (5)	0.6243 (4)	0.1953 (8)	0.049
C(3)	0.7862 (4)	0.6279 (3)	0.1853 (8)	0.052
C(4)	0.6806 (6)	0.6264 (3)	-0.0080 (8)	0.050
C(5)	0.7186 (5)	0.6219 (3)	-0.1175 (9)	0.046
C(11)	0.9256 (6)	0.6163 (6)	-0.0468 (10)	0.056
C(12)	1.0189 (6)	0.6245 (6)	0.3713 (10)	0.064
C(13)	0.7883 (7)	0.6323 (6)	0.3490 (10)	0.072
C(14)	0.5524 (6)	0.6290 (6)	-0.0828 (11)	0.067
C(15)	0.6373 (6)	0.6191 (6)	-0.3275 (11)	0.058
C(6)	0.6554 (4)	0.1522 (4)	-0.1498 (8)	0.047
C(7)	0.7606 (5)	0.1497 (3)	-0.1356 (8)	0.045
C(8)	0.7201 (5)	0.1432 (3)	-0.3241 (7)	0.045
C(9)	0.5898 (5)	0.1416 (3)	-0.4549 (9)	0.046
C(10)	0.5498 (5)	0.1471 (3)	-0.3472 (7)	0.048
C(16)	0.6557 (6)	0.1589 (6)	0.0136 (10)	0.057
C(17)	0.8908 (6)	0.1534 (6)	0.0454 (10)	0.053
C(18)	0.8002 (6)	0.1388 (5)	-0.3757 (10)	0.051
C(19)	0.5091 (6)	0.1352 (6)	-0.6677 (7)	0.055
C(20)	0.4198 (6)	0.1476 (6)	-0.4271 (10)	0.058

Table 2. Selected intramolecular distances ( $\text{\AA}$ ) and bond angles ( $^\circ$ )

A. $[\text{Co}_2(\eta^5\text{-C}_5\text{Me}_5)_2(\mu_2\text{-Cl})_3]^+$ monocation (Ic)			
Co(1)⋯Co(2)	2.914 (2)	Cl(4)⋯Cl(6)	3.144 (4)
Cl(4)⋯Cl(5)	3.152 (4)	Cl(5)⋯Cl(6)	3.115 (4)
Co(1)—Cl(4)	2.337 (3)	Co(2)—Cl(4)	2.337 (3)
Co(1)—Cl(5)	2.315 (3)	Co(2)—Cl(5)	2.313 (3)
Co(1)—Cl(6)	2.321 (3)	Co(2)—Cl(6)	2.324 (3)
Co(1)—C(1)	2.085 (5)	Co(2)—C(6)	2.066 (5)
Co(1)—C(2)	2.074 (5)	Co(2)—C(7)	2.082 (5)
Co(1)—C(3)	2.066 (5)	Co(2)—C(8)	2.091 (5)
Co(1)—C(4)	2.072 (5)	Co(2)—C(9)	2.081 (5)
Co(1)—C(5)	2.084 (5)	Co(2)—C(10)	2.066 (5)
C(1)—C(2)	1.428 (6)	C(6)—C(7)	1.433 (5)
C(2)—C(3)	1.428 (6)	C(7)—C(8)	1.433 (5)
C(3)—C(4)	1.428 (6)	C(8)—C(9)	1.433 (5)
C(4)—C(5)	1.428 (6)	C(9)—C(10)	1.433 (5)
C(5)—C(1)	1.428 (6)	C(10)—C(6)	1.433 (5)
C(1)—C(11)	1.498 (7)	C(6)—C(16)	1.503 (7)
C(2)—C(12)	1.498 (7)	C(7)—C(17)	1.503 (7)
C(3)—C(13)	1.498 (7)	C(8)—C(18)	1.503 (7)
C(4)—C(15)	1.498 (7)	C(9)—C(19)	1.503 (7)
C(5)—C(14)	1.498 (7)	C(10)—C(20)	1.503 (7)
Co(1)—Cl(4)—Co(2)	77.2 (1)	Co(1)—Cl(6)—Co(2)	77.7 (1)
Co(1)—Cl(5)—Co(2)	78.1 (1)		
Cl(4)—Co(1)—Cl(5)	85.3 (1)	Cl(4)—Co(2)—Cl(5)	85.4 (1)
Cl(4)—Co(1)—Cl(6)	84.9 (1)	Cl(4)—Co(2)—Cl(6)	84.8 (1)
Cl(6)—Co(1)—Cl(5)	84.4 (1)	Cl(5)—Co(2)—Cl(6)	84.4 (1)
B. $[\text{Co}_2\text{Cl}_4(\mu_2\text{-Cl})_2]^{2-}$ dianion (Ia)			
Co(3)⋯Co(3')	3.366 (3)	Cl(1)⋯Cl(1')	3.360 (6)
Co(3)—Cl(1)	2.386 (3)	Cl(2)⋯Cl(3)	3.719 (5)
Co(3)—Cl(1')	2.370 (3)	Cl(2)⋯Cl(1)	3.835 (4)
Co(3)—Cl(2)	2.216 (3)	Cl(2)⋯Cl(1')	3.843 (4)
Co(3)—Cl(3)	2.224 (4)	Cl(3)⋯Cl(1)	3.839 (5)
		Cl(3)⋯Cl(1')	3.800 (5)
Cl(2)—Co(3)—Cl(1)	112.8 (1)	Cl(1)—Co(3)—Cl(1')	89.9 (1)
Cl(2)—Co(3)—Cl(1')	113.8 (1)	Cl(2)—Co(3)—Cl(3)	113.8 (1)
Cl(3)—Co(3)—Cl(1)	112.7 (1)	Cl(3)—Cl(1)—Co(5)	90.1 (1)
Cl(3)—Co(3)—Cl(1')	111.6 (1)		

(a) *The  $[\text{Co}_2(\eta^5\text{-C}_5\text{Me}_5)_2(\mu_2\text{-Cl})_3]^+$  monocation (Ic).* Based on the premise that each  $\text{C}_5\text{Me}_5^-$  ligand occupies three coordination sites, the architecture (Fig. 1) of (Ic) may be visualized as two congruent  $(\text{C}_5\text{Me}_5)\text{CoCl}_3$  octahedra sharing a common trichloride face. The eclipsed conformation of the two  $\text{C}_5\text{Me}_5^-$  ligands gives rise to the (Ic) pseudo  $mm2$  ( $C_{2v}$ ) geometry with one vertical mirror plane (which bisects each  $\text{C}_5\text{Me}_5^-$  ring) passing through Cl(4) and both cobalt atoms and the other vertical mirror passing through the three bridging chlorides. If each  $\text{C}_5\text{Me}_5^-$  ligand is assumed to possess cylindrical symmetry, the resulting geometry ideally has  $\bar{6}2m$  ( $D_{3h}$ ) symmetry. This 36-electron system composed of two formal  $d^6$   $\text{Co}^{\text{III}}$  configurations does not necessitate any electron-pair coupling interaction in accordance with the observed nonbonding Co(1)⋯Co(2) distance of 2.914 (2)  $\text{\AA}$ . The mean planes for the five ring carbon atoms in the two independent  $\text{C}_5\text{Me}_5^-$  ligands are essentially parallel with each other (1.8° deviation) and with the trichloride plane (0.7 and 1.1° deviations).

(Ic) has been the subject of only one brief report (Kolle, Khouzami & Fuss, 1982) outlining its synthesis from the reaction of  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$  with  $\text{C}_5\text{Me}_5\text{Li}$  followed by an *in situ* oxidation with  $\text{FeCl}_3$ . The rhodium analogue of (Ic) was previously isolated from the reaction of  $\text{Rh}_2(\eta^5\text{-C}_5\text{Me}_5)_2(\mu_2\text{-Cl})_2$  with sodium tetraphenylborate (Kang & Maitlis, 1971). Of prime interest is the closely related ethyltetramethylcyclopentadienyl  $[\text{Co}_2(\eta^5\text{-C}_5\text{Me}_4\text{Et})_2(\mu_2\text{-Cl})_3]^+$  monocation (IIc), crystallographically determined as the  $[\text{FeCl}_4]^-$  salt by Couldwell & Husain (1978), which was synthesized by Green & Pardy (1979) from an intensely blue dichloromethane soluble compound of empirical formula  $\text{Co}_3(\text{C}_5\text{Me}_4\text{Et})_2\text{Cl}_6$  but of unknown structure. This chemical precursor, prepared in excellent yield (84%) by the reaction of cobalt(II) chloride and  $\text{Sn}(\text{C}_5\text{Me}_4\text{Et})(n\text{-Bu})_3$  followed by treatment with

dry  $\text{Cl}_2$ , was shown by Green & Pardy (1979) to be a highly useful starting material for a large variety of other organocobalt complexes. Their effort to characterize this compound structurally was unsuccessful because the crystals examined by X-ray diffraction were twinned. On the basis of the structure of (I), together with the close similarity of its color, solubility behavior and paramagnetic broadening of the  $^1\text{H}$  NMR spectrum with that of  $\text{Co}_3(\text{C}_5\text{Me}_4\text{Et})_2\text{Cl}_6$ , there is no doubt in our minds that the structure of the Green-Pardy compound is the corresponding ethyltetramethylcyclopentadienyl derivative,  $[\text{Co}_2(\eta^5\text{-C}_5\text{Me}_4\text{Et})_2(\mu_2\text{-Cl})_3]^+[\text{Co}_2\text{Cl}_4(\mu_2\text{-Cl})_2]^{2-}$ , of (I).

A comparison (Table 3) of the mean geometrical parameters for the  $\text{Co}(\text{Cl}_b)_3\text{Co}'$  core of (Ic) with that of (IIc) reveals that (IIc) has significantly shorter  $\text{Co}-\text{Cl}_b$  bond lengths (by 0.05 Å), which may have an electronic origin. However, the smaller  $\text{Cl}_b\cdots\text{Cl}'_b$  contacts in (IIc) [3.042 Å (av.)] than those in (Ic) [3.137 Å (av.)] result in larger  $\text{Co}-\text{Cl}_b-\text{Co}'$  bond angles in (IIc) [78.8° (av.)] than those in (Ic) [77.6° (av.)], which in a compensatory fashion give rise to the nonbonding  $\text{Co}\cdots\text{Co}'$  distance of 2.887(2) Å in (IIc) being only 0.027 Å shorter than that in (Ic). These observed structural variations in both (Ic) and (IIc) are entirely consistent with a marked axial elongation of the  $\text{Co}(\text{Cl}_b)_3\text{Co}'$  core due to a net  $\text{Co}\cdots\text{Co}'$  repulsion. This axial distortion is in accordance with a systematic correlation by Cotton & Ucko (1972) of structural parameters with electronic configurations of the metal atoms in a number of confacial bioctahedral  $M_2X_9$  structures including the electronically equivalent  $[\text{Rh}_2\text{Cl}_6]^{3-}$  trianion whose  $\text{Rh}(\text{Cl}_b)_3\text{Rh}'$  core with two  $d^6$   $\text{Rh}^{\text{III}}$  atoms is analogously elongated.

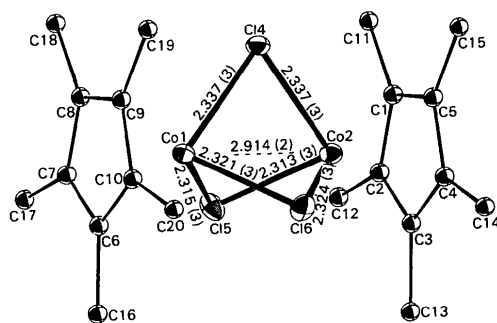


Fig. 1. The confacial bioctahedral geometry of the  $\text{Co}^{\text{III}}\cdots\text{Co}^{\text{III}}$  nonbonding  $[\text{Co}_2(\eta^5\text{-C}_5\text{Me}_5)_2(\mu_2\text{-Cl})_3]^+$  monocation (Ic), which has crystallographic 1 ( $C_1$ ) site symmetry. The atomic thermal ellipsoids are drawn at the 20% probability level.

Table 3. Comparison of selected geometrical parameters for the pentamethylcyclopentadienyl  $[\text{Co}_2(\eta^5\text{-C}_5\text{Me}_5)_2(\mu_2\text{-Cl})_3]^+$  monocation (Ic) and ethyltetramethylcyclopentadienyl  $[\text{Co}_2(\eta^5\text{-C}_5\text{Me}_4\text{Et})_2(\mu_2\text{-Cl})_3]^+$  monocation (IIc) and for the centrosymmetric  $[\text{Co}_2\text{Cl}_4(\mu_2\text{-Cl})_2]^{2-}$  dianion (Ia), (IIIa) of different salts (I), (II), (III)

	(Ic)*	(IIc)†	(Ia)*	(IIIa)‡
<b>A. Distances (Å)</b>				
$\text{Co}\cdots\text{Co}$	2.914 (2)	2.887 (2)	3.366 (3)	3.277 (6)
$\text{Co}-\text{Cl}_l$	Mean —	—	2.220	2.233
	Range —	—	2.216 (3), 2.224 (4)	2.227 (7), 2.238 (6)
$\text{Co}-\text{Cl}_b$	Mean 2.324	2.274	2.378	2.336
	Range 2.313 (3)–2.337 (3)	2.251 (5)–2.297 (5)	2.370 (3), 2.386 (3)	2.329 (5), 2.342 (6)
$\text{Cl}_b\cdots\text{Cl}'_b$	Mean 3.137	3.042	3.360 (6)	3.328
	Range 3.115 (4)–3.152 (4)	3.021 (7)–3.054 (7)	—	—
$\text{Cl}_l\cdots\text{Cl}'_l$	—	—	3.719 (5)	3.779
<b>B. Bond angles (°)</b>				
$\text{Co}-\text{Cl}_b-\text{Co}'$	Mean 77.6	78.8	90.1 (1)	89.1 (2)
	Range 77.2 (1)–78.1 (1)	78.3 (2)–79.7 (2)	—	—
$\text{Cl}_b-\text{Co}-\text{Cl}'_b$	Mean 84.9	84.0	89.9 (1)	90.9 (2)
	Range 84.4 (1)–85.4 (1)	82.7 (3)–84.7 (2)	—	—
$\text{Cl}_l-\text{Co}-\text{Cl}'_l$	Mean —	—	113.8 (1)	115.7 (3)
	Range —	—	—	—
$\text{Cl}_l-\text{Co}-\text{Cl}_b$	Mean —	—	112.7	111.9
	Range —	—	111.6 (1)–113.8 (1)	107.1 (3)–114.5 (3)

\*  $[\text{Co}_2(\eta^5\text{-C}_5\text{Me}_5)_2(\mu_2\text{-Cl})_3]^+[\text{Co}_2\text{Cl}_4(\mu_2\text{-Cl})_2]^{2-}$  (I); this work.

†  $[\text{Co}_2(\eta^5\text{-C}_5\text{Me}_4\text{Et})_2(\mu_2\text{-Cl})_3]^+[\text{FeCl}_4]^-$  (II); Couldwell & Husain (1978).

‡  $[\text{Co}_2\text{N}_6\text{P}_6(\text{NMe}_2)_{12}\text{Cl}]^{2-}[\text{Co}_2\text{Cl}_4(\mu_2\text{-Cl})_2]^{2-}\cdot 2\text{CHCl}_3$  (III); Harrison & Trotter (1973).

(b) The [Co<sub>2</sub>Cl<sub>4</sub>(μ<sub>2</sub>-Cl)<sub>2</sub>]<sup>2-</sup> dianion (Ia). The [Co<sub>2</sub>Cl<sub>6</sub>]<sup>2-</sup> dianion (Fig. 2) of crystallographic  $\bar{1}(C_2)$  site symmetry with a tetrahedral coordination about each *d*<sup>7</sup> Co<sup>II</sup> atom is also uncommon. This crystallographic study provides only the second example for the solid-state existence of the trichlorocobaltate(II) monoanion as a dimeric dianion with a dichloro-shared bitetrahedral geometry; its entity was initially recognized from the previously determined crystal structure (Harrison, Paddock, Trotter & Wingfield, 1972; Harrison & Trotter, 1973) of it (IIIa) as the [Co{N<sub>6</sub>P<sub>6</sub>(NMe<sub>2</sub>)<sub>12</sub>}Cl]<sup>+</sup> salt (III), which was unexpectedly isolated from the reaction of cobalt(II) chloride with dodeca(dimethylamino)cyclohexaphosphazene. As part of a theoretical investigation of a wide variety of edge-shared bitetrahedral *M*<sub>2</sub>L<sub>6</sub> dimers, Summerville & Hoffmann (1976) performed MO calculations on the [Co<sub>2</sub>Cl<sub>6</sub>]<sup>2-</sup> dianion (IIIa) but were not able to predict the extent of magnetic coupling of the two *d*<sup>7</sup> Co<sup>II</sup> atoms. However, a magnetic susceptibility measurement (Paul, Sharma & Verma, 1974, 1976) of this dianion, formed as the [S<sub>4</sub>N<sub>3</sub>]<sup>+</sup> salt in the reaction of thiotriethiazyl chloride with cobalt(II) chloride, has yielded a room-temperature magnetic moment of 4.3μ<sub>B</sub>. This value is within the 4.4–4.8μ<sub>B</sub> range for a high-spin tetrahedral *d*<sup>7</sup> Co<sup>II</sup> atom with a <sup>4</sup>A<sub>2</sub> ground state under localized cubic  $\bar{4}3m(T_d)$  symmetry (Figgis & Lewis, 1964).

An inspection of Table 3 reveals distinct structural differences between (Ia) and (IIIa) including a 0.089 Å-longer nonbonding Co...Co' distance in (Ia) [3.366 (3) Å] than in (IIIa) [3.277 (6) Å], which in part is a consequence of the 0.042 Å-longer Co–Cl<sub>b</sub> bond lengths in (Ia). The close conformity of both the Co–Cl<sub>b</sub>–Co' and Cl<sub>b</sub>–Co–Cl<sub>b</sub>' bond angles to 90° values in the exactly planar (centrosymmetric) Co<sub>2</sub>Cl<sub>2</sub> ring system of (Ia) and (IIIa) is also in accordance with such *M*<sub>2</sub>X<sub>2</sub> ring systems containing no direct 'attractive' metal–metal interactions (Dahl, Rodulfo de Gil & Feltham, 1969). Although there is no apparent

rationalization (other than different packing environments) for the highly significant geometrical variations of the same dianion [(Ia) and (IIIa)] in two different salts [(I) and (III)], Harrison & Trotter (1973) pointed out that the chloride atoms in (IIIa) exhibit unusually large thermal ellipsoids (corresponding to maximum r.m.s. displacements of ca 0.5 Å), which are presumably a consequence of a librational motion and/or crystal disorder.

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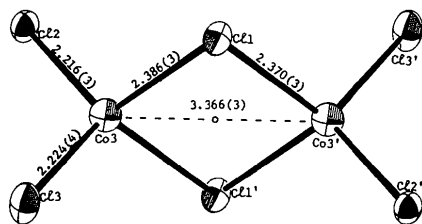


Fig. 2. The edge-shared bitetrahedral geometry of the Co<sup>II</sup>...Co<sup>II</sup> nonbonding [Co<sub>2</sub>Cl<sub>4</sub>(μ<sub>2</sub>-Cl)<sub>2</sub>]<sup>2-</sup> dianion (Ia), which possesses crystallographic  $\bar{1}(C_2)$  site symmetry and which experimentally conforms to *mmm* (*D*<sub>2h</sub>) symmetry. The atomic thermal ellipsoids are drawn at the 20% probability level.