Table 3. *Electron populations of the* O *atoms in* (a) *chlorite and* (b) *nitrite ions based on the STO-3G basis set*

The y axis is perpendicular to the molecular plane and z along the twofold axis.

	$1s$	$2s$	$2p_x$	$2p_y$	$2p_z$	Total
(a)	1·99960	1·96633	1·01883	2·00000	1·54695	8·53171
(b)	1·99853	1·87826	1·34251	1·50068	1·73160	8·45158

& Schempp, 1975) and $Zn(ClO_2)_2.2H_2O$ (Pakkanen, 1979). The neighboring metal cations are shifted by 1·541 (1)–2·191 (2) Å from the ClO_2^- plane and the projections of the metal atoms on the ClO_2^- plane approximately lie on an extension of the Cl—O bond axis. Except for (III) there are no metal cations or water molecules on the ClO_2^- plane in contrast to the nitrite salts in which there are metal cations nearly on the NO_2^- plane. Experimental and theoretical deformation density in NO_2^- suggested that the metal cations approach the sp^2 lone-pair lobes of the N and O atoms in the molecular plane (Ohba, Kikkawa & Saito, 1985; Kikkawa, Ohba, Saito, Kamata & Iwata, 1987). In order to investigate the difference in preferred location of the metal cations relative to the chlorite and nitrite ions, the theoretical deformation density of ClO_2^- was calculated by an *ab initio* molecular-orbital method using the MIDI4* basis set as reported previously (Kikkawa, Ohba, Saito, Kamata & Iwata, 1987). The theoretical deformation densities of NO_2^- and ClO_2^- are compared in Fig. 3, where the reference density is the superposition of the neutral independent atom densities. The positive deformation density of the terminal O atoms in the ClO_2^- plane is much lower than that of NO_2^-. On the other hand, electron density in the π region of the O atom is much higher for ClO_2^- than for NO_2^-. The electron populations calculated by using the STO-3G basis set are compared in Table 3. The oxygen $2p_y$ orbital perpendicular to the ClO_2^- plane is fully occupied. This is the electron-rich orbital in the ClO_2^- ion, to which metal cations or water H atoms preferably approach as seen in Fig. 2. In conclusion, the coloration of chlorite ion seems to be caused by the perturbation of the lone-pair π orbitals of the terminal O atoms by the post-transition-metal cations.

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Structure of Dichlorobis(tetracarbonylcobaltio)tin(IV)(2 *Co–Sn*)

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Abstract. $SnCl_2[Co(CO)_4]_2$, $M_r = 531·5$, monoclinic, $P2_1/c$, $a = 11·716$ (4), $b = 11·486$ (4), $c = 12·765$ (8) Å, $\beta = 108·42$ (3)°, $U = 1630$ (1) Å³, $Z = 4$, $D_x = 2·17$ g cm⁻³, $\lambda(Mo~K\alpha) = 0·7107$ Å, $\mu = 36·8$ cm⁻¹, $F(000) = 1000$, $T = 293$ K, $R = 0·045$ for 2558 $[I > 2\sigma(I)]$ reflections. The Sn atom is bonded to two Cl atoms [Sn—Cl (av.) = 2·368 (2) Å, Cl—Sn—Cl = 101·3 (1)°] and to two $Co(CO)_4$ groups [Sn—Co (av.) = 2·534 (1) Å, Co—Sn—Co = 129·3 (1)°].

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Table 1. *Final positional and equivalent isotropic thermal parameters for* Cl₂Sn[Co(CO)₄]₂

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U_{eq}(\text{Å}^2)$
Sn(1)	0·77920 (3)	0·16878 (4)	0·64689 (3)	0·042
Co(1)	0·9863 (1)	0·1726 (1)	0·7895 (1)	0·045
Co(2)	0·5747 (1)	0·1868 (1)	0·6738 (1)	0·047
Cl(1)	0·7812 (2)	0·3142 (2)	0·5153 (2)	0·077
Cl(2)	0·7717 (2)	−0·0030 (2)	0·5430 (2)	0·073
C(1)	1·0378 (5)	0·1717 (6)	0·6689 (5)	0·052
O(1)	1·0733 (4)	0·1734 (4)	0·5979 (4)	0·071
C(2)	0·9423 (5)	0·3127 (6)	0·8301 (5)	0·055
O(2)	0·9176 (4)	0·4005 (5)	0·8540 (4)	0·083
C(3)	1·1360 (6)	0·1730 (6)	0·8894 (6)	0·068
O(3)	1·2994 (4)	0·1729 (5)	0·9500 (5)	0·102
C(4)	0·9423 (6)	0·0391 (7)	0·8394 (5)	0·061
O(4)	0·9186 (5)	−0·0459 (5)	0·8726 (5)	0·090
C(5)	0·5175 (5)	0·1700 (6)	0·5258 (6)	0·063
O(5)	0·4803 (5)	0·1609 (5)	0·4334 (5)	0·097
C(6)	0·4297 (6)	0·1961 (6)	0·6944 (6)	0·062
O(6)	0·3390 (5)	0·2014 (5)	0·7080 (5)	0·092
C(7)	0·6185 (5)	0·0599 (7)	0·7590 (5)	0·056
O(7)	0·6407 (4)	−0·0206 (5)	0·8130 (4)	0·085
C(8)	0·6204 (6)	0·3308 (7)	0·7237 (6)	0·067
O(8)	0·6443 (5)	0·4238 (5)	0·7529 (6)	0·107

Table 2. *Selected bond lengths* (Å) *and angles* (°) *for* Cl₂Sn[Co(CO)₄]₂

Sn(1)—Co(1)	2.533 (1)	Sn(1)—Co(2)	2·535 (1)
Sn(1)—Cl(1)	2.373 (2)	Sn(1)—Cl(2)	2·363 (2)

Co(1)—Sn(1)—Co(2)	129·3 (1)	Sn(1)—Co(2)—C(6)	178·5 (2)
Co(1)—Sn(1)—Cl(1)	106·0 (1)	Sn(1)—Co(2)—C(7)	84·9 (2)
Co(1)—Sn(1)—Cl(2)	106·0 (1)	Sn(1)—Co(2)—C(8)	86·1 (2)
Co(2)—Sn(1)—Cl(1)	105·0 (1)	Co(1)—Sn(1)—Cl(2)	106·0 (1)
Cl(1)—Sn(1)—Cl(2)	101·3 (1)	Sn(1)—Co(1)—C(1)	84·0 (2)
Sn(1)—Co(1)—C(2)	85·7 (2)	Sn(1)—Co(1)—C(3)	178·7 (3)
Sn(1)—Co(1)—C(4)	85·5 (2)		

Introduction. We have recently prepared a series of cobalt carbonyl anions incorporating chloro–stannyl units (Curnow & Nicholson, 1984; Curnow, Nicholson & Severinsen, 1990). These appear to have exceptionally short Sn—Co bond lengths, but reliable comparative structural data are sparse (Mackay & Nicholson, 1982; Zubieta & Zuckerman, 1978). Cl₃SnCo(CO)₄ has not been reported, while the study of ClSn[Co(CO)₄]₃ (Biryukov *et al.*, 1971; Sn—Co 2·58–2·62 Å, Sn—Cl 2·54 Å) is not a precise one; the Sn—Cl bond appears surprisingly long. To provide accurate benchmark values for Sn—Co and Sn—Cl bonds, and to extend the series of structures of the type Cl₂Sn*ML*ₙ, we have now determined the structure of Cl₂Sn[Co(CO)₄]₂.

Experimental. Red crystals of Cl₂Sn[Co(CO)₄]₂ [from Co₂(CO)₈ and SnCl₂ (Patmore & Graham, 1966)] were grown from hexane at 258 K. Preliminary precession photography established monoclinic symmetry and systematic absences uniquely defining the space group $P2_1/c$. Nicolet $P3$ automated diffractometer, graphite monochromator, lattice parameters from 25 high-angle reflections auto-

matically centered; 3858 reflections, 3735 unique [R(merge) = 0·0165], $4 < 2\theta < 55°$, collected using Wyckoff peak-top scans, $0 < h < 16$, $0 < k < 15$, $-17 < l < 17$; three standard reflections monitored regularly showed no significant variation; 2567 data [$I > 2\sigma(I)$] corrected for Lorentz and polarization effects, empirical absorption correction applied based on a series of ψ scans, crystal size $0·6 \times 0·5 \times 0·5$ mm, transmission factors between 0·766 and 0·891. Structure solved by direct methods; full-matrix least-squares refinement based on F with all atoms anisotropic converged with $R = 0·0434$, $wR = 0·0334$ with $w = [\sigma^2(F) + 0·00006F^2]^{-1}$, isotropic extinction coefficient 0·00365, $(\Delta/\sigma)_{max} = 0·06$, final difference map showed one peak $1·0 \, e \, \text{Å}^{-3}$ adjacent to the Sn atom; atomic scattering factors and f' and f'' values from *International Tables for X-ray Crystallography* (1974). Calculations with *SHELXS*86 and *SHELX*76 (Sheldrick 1976, 1986). Atomic positional parameters are listed in Table 1* and selected bond lengths and angles are given in Table 2.

Discussion. The structure shows individual molecules of Cl₂Sn[Co(CO)₄]₂, as illustrated in Fig. 1. The Sn atom is bonded in a markedly distorted tetrahedral fashion to two Cl atoms and two Co(CO)₄ groups. Each of the cobalt atoms is in an approximately trigonal-bipyramidal coordination, with the equatorial carbonyl groups bent in the usual 'umbrella' fashion towards the tin substituent, with the average Sn—Co—C$_{eq}$ angle 85·2°.

There is now a series of structures of the type Cl₂Sn[ML_n]₂ with ML_n = Cr(CO)₃Cp, Mn(CO)₅, Fe(CO)₂Cp, Co(CO)₄ and Co(CO)₂ (norbornadiene) (Cp = cyclopentadienyl), and structural parameters are summarized in Table 3 for comparison.

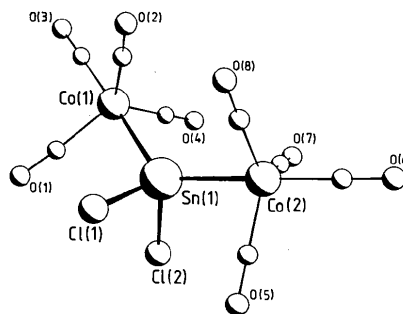The Sn—Co bond length in Cl₂Sn[Co(CO)₄]₂, average 2·534(1) Å, is consistent with a shortening of

Fig. 1. A perspective view of Cl₂Sn[Co(CO)₄]₂.

Table 3. *Selected bond lengths (Å) and angles (°) for complexes of the type* $Cl_2Sn[ML_n]_2$

ML_n	Sn—M^*	M—Sn—M^*	Sn—Cl^*	Cl—Sn—Cl^*	Ref.
Co(CO)₄	2·534 (1)	129·3 (1)	2.368 (2)	101·3 (1)	This work
Co(CO)₂(nbd)†	2·498 (1)	128·3 (1)	2·410 (2)	98·1 (1)	(1)
Fe(CO)₂Cp	2·492 (8)	128·6 (3)	2·43 (1)	94·1 (6)	(2)
Mn(CO)₅	2·635 (2)	126·2 (1)	2·385 (2)	95·8 (1)	(3)
Cr(CO)₃Cp	2·697 (2)	130·2 (1)	2·417 (3)	95·0 (1)	(4)

References: (1) Boer & Flynn (1971); (2) O'Connor & Corey (1967); (3) Preut, Wolfes & Haupt (1975); (4) Stephens (1975).

* Average values.
† nbd = norbornadiene.

the Sn—M bond going from M = Cr→Mn→Co as the atomic radius of the metal atom decreases across the series. The Sn—Fe value for $Cl_2Sn[Fe(CO)_2Cp]_2$ (O'Connor & Corey, 1967) appears smaller than expected from this trend, even allowing for the effect of the Cp ligand. Comparison of the Sn—Co bond value for $Cl_2Sn[Co(CO)_4]_2$ with that of the substituted $Cl_2Sn[Co(CO)_2(nbd)]_2$ (nbd = norbornadiene) (Boer & Flynn, 1971) shows that there is a significant contraction [0·036 (2) Å] on replacing the CO ligand opposite the Sn—Co bond by a η^2-C=C group; this is yet another example of the relatively strong *trans* influence of a CO ligand in these complexes (Curnow, Nicholson & Severinsen, 1990). For all of the examples given in Table 3 the M—Sn—M bond angles are much greater than the tetrahederal angle, but the overall range (126·3–130·2°) is surprisingly small considering the variation in steric properties of the ML_n groups. This suggests an electronic rationale, with the Sn—M bonds having enhanced s-orbital character (leaving the M—Cl with enhanced p-orbital contributions) because of the differing electronegativities of the atoms bonded to tin [*i.e.* isovalent hybridization (Bent, 1961)].

The Sn—Cl bond lengths in $Cl_2Sn[Co(CO)_4]_2$ average 2·368 (2) Å, which is marginally shorter than any of the other examples in Table 3, although variations

are not marked. The Cl—Sn—Cl angle in $Cl_2Sn[Co(CO)_4]_2$ is also wider at 101·3 (1)° than for other $Cl_2Sn(ML_n)_2$, although all are significantly less than the tetrahedral angle. While these values are generally consistent with the isovalent hybridization ideas, there does not appear to be any correlation at the more detailed level relating trends in Sn—Cl, Sn—M and Cl—Sn—Cl parameters.

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On the Structure of 'Potassium Nitroprusside 0·8 Hydrate'

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Abstract. The crystal structure of the compound reported as $K_2[Fe(CN)_5NO].0.8H_2O$, potassium pentacyanonitrosylferrate hydrate (1/0·8), recently described and refined in the non-centrosymmetric space group $Pna2_1$ [orthorhombic; a = 30·000 (8), b = 11·272 (3), c = 16·053 (4) Å, Z = 20; Castellano,

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