Data collection

Rigaku AFC-4*R* diffractometer
ω scans
Absorption correction:
  ψ scan (North *et al.*, 1968)
  $T_{\min} = 0.860$, $T_{\max} = 0.898$
8640 measured reflections
7964 independent reflections
3558 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.023$
$\theta_{\max} = 27.5°$
$h = 0 \rightarrow 25$
$k = 0 \rightarrow 23$
$l = -16 \rightarrow 16$
3 standard reflections every 150 reflections
  intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.086$
$S = 0.842$
6646 reflections
415 parameters
H-atom parameters constrained
$w = 1/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.398$ e Å^{-3}
$\Delta\rho_{\min} = -0.429$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Sn1—Sn2	4.2793 (11)	Sn2—C3	2.138 (7)
Sn1—C1	2.135 (7)	Sn2—C4	2.138 (7)
Sn1—C2	2.117 (7)	Sn2—C16	2.153 (7)
Sn1—C5	2.151 (6)	Sn2—C36	2.149 (7)
Sn1—C25	2.150 (7)		
C2—Sn1—C1	107.9 (3)	C3—Sn2—C4	108.5 (3)
C1—Sn1—C5	106.8 (3)	C3—Sn2—C36	109.6 (3)
C1—Sn1—C25	105.9 (3)	C4—Sn2—C36	108.2 (3)
C2—Sn1—C5	109.4 (3)	C3—Sn2—C16	107.4 (3)
C2—Sn1—C25	107.4 (3)	C4—Sn2—C16	106.1 (3)
C25—Sn1—C5	118.9 (2)	C36—Sn2—C16	116.8 (3)

All H atoms were located at ideal positions with C—H = 0.96 (sp^3-hybridized geometry) or 0.93 Å (sp^2-hybridized geometry) and included in the refinement, but were restrained to ride on their bonded atoms. The isotropic displacement parameters of the H atoms were held fixed at $1.2U_{\rm eq}$ of their riding atoms. F_o data were collected and all calculations were carried out on an NEC EWS 4800/410 workstation at the Research Centre for Protein Engineering, Institute for Protein Research, Osaka University, Japan.

Data collection: Rigaku AFC-4*R* software. Cell refinement: Rigaku AFC-4*R* software. Data reduction: Rigaku AFC-4*R* software. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1135). Services for accessing these data are described at the back of the journal.

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Bis[tris(2-aminoethyl)amine]cobalt(II) Bis[tetracarbonylcobaltate(1−)]

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Abstract

The title compound, $[Co(C_6H_{18}N_4)_2][Co(CO)_4]_2$, comprises $[Co(N_4H_{18}C_6)_2]^{2+}$ and $[Co(CO)_4]^-$ ions. The cation presents a distorted-octahedral arrangement of N atoms around the Co^{II} atom, while in the anion, four CO ligands are coordinated to the Co^{-I} atom in an approximately tetrahedral distribution. The anions and cations are linked in the crystal structure *via* hydrogen bonds of the type Co^{II}—*X*—H···OC—Co^{-I} (*X* = N or C), in which both donor and acceptor groups are influenced by the coordination to a metal center.

Comment

In recent years, we have been investigating hydrogen-bonding interactions involving organometallic species (Brammer *et al.*, 1991, 1992, 1995; Brammer & Zhao, 1994; Zhao *et al.*, 1996). This interest led us to systematically study hydrogen-bonding interactions involving the tetracarbonylcobaltate(1−) anion, $[Co(CO)_4]^-$ (Brammer & Mareque Rivas, 1998). This anion possesses two types of atom which can act as acceptor sites for the formation of hydrogen bonds: (i) the electron-rich d^{10} Co^{-1} metal center and (ii) the O atoms of the metal-bound carbonyl groups. In the cases we have reported to date, the hydrogen-bond donors have been the N—H and C—H groups present in a variety of alkylammonium cations $[R_3NH]^+$. In these organometallic salts of formula $[R_3NH]^+[Co(CO)_4]^-$, the hydrogen bonds can be placed into two categories based upon the role played by the metal. In the first type, typified by N—H···Co, the metal directly participates as the acceptor group. In the second type, X—H···OC—Co (X = C, N), the transition metal atom participates indirectly in the hydrogen bond since coordination of the π-acid CO ligand to the metal affects the basicity of the O atom. However, in the present study, we can consider a third case in which both the hydrogen-bond donor and acceptor are influenced by the transition metal center.

Similar to what we found in species of formula $[R_3NH]^+[Co(CO)_4]^-$, the hydrogen bonds occur between the anions and cations. However, in (1), since both the donor N—H and C—H groups of the cation, and the acceptor CO groups of the anion are part of ligands which are covalently bound to a metal atom, herein Co^{II} and Co^{-1}, respectively, both the donor and acceptor should be influenced to some degree by the metal.

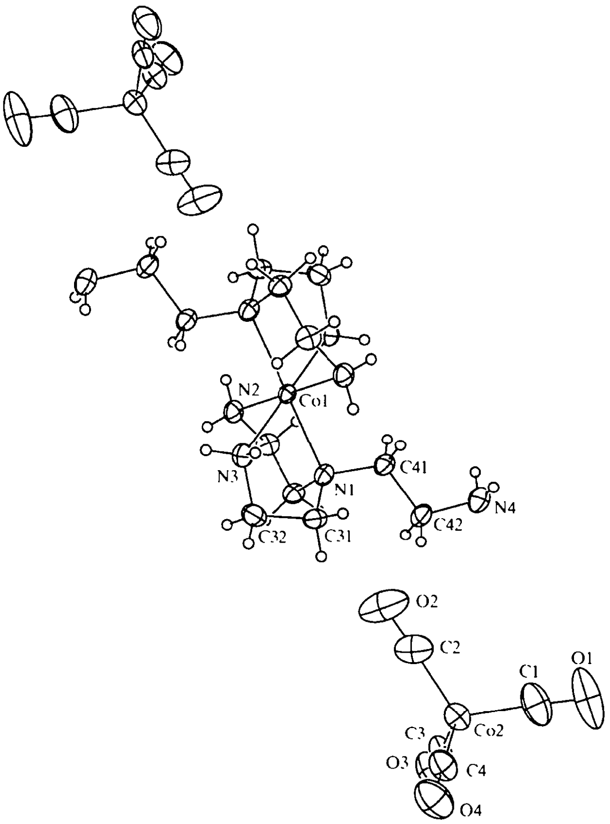
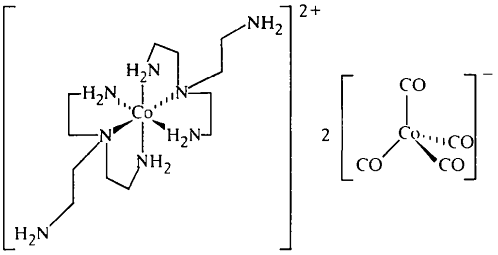


Fig. 1. View of $[Co(tren)_2][Co(CO)_4]_2$ showing the labeling of the non-H atoms, with ellipsoids shown at the 50% probability level. The minor disordered component of the cation is not shown.



(1)

The molecular structure of (1) is shown in Fig. 1. In the centrosymmetric cation, two tren ligands [tren is tris(2-aminoethyl)amine] are coordinated to the Co^{II} center in a tridentate manner. The arrangement of N atoms around the metal is a slightly distorted octahedral geometry which can be explained on the basis of the strain associated with the five-membered chelating bridge. The Co^{II}—N bond lengths are well within the range found for similar compounds (Orpen *et al.*, 1989). The molecular structure of the title compound also contains two approximately tetrahedral $[Co(CO)_4]^-$ anions.

However, the most interesting structural feature is the set of hydrogen bonds between anions and cations, in which the proximity to a metal may affect both the donor and acceptor atoms. Each of the anions interacts with three surrounding cations *via* two N—H···O and two C—H···O hydrogen bonds (Fig. 2 and Table 2), involving all carbonyl O atoms. The N···O separations are shorter than the C···O separations, as one might anticipate. The latter are typical of the values observed in related structures containing the $[Co(CO)_4]^-$ anion (Brammer & Mareque Rivas, 1998). However, these separations are at the short end of the range of C—H···O separations found in recent surveys of such interactions in first row metal terminal carbonyl complexes (Braga *et al.*, 1995; Braga & Grepioni, 1997). This observation can be explained based on two facts associated with the anionic nature of the metal carbonyl complex: (i) the anionic character results in greater π-back donation from the metal to the CO ligands, increasing the basicity of the O atoms, and (ii) since in the hydrogen-bonding interactions the electrostatic component predominates, in the title compound, one could expect enhanced hydrogen-bond strength because of the cation–anion electrostatic attractive interaction. Braga *et al.* (1997) have described such hydrogen bonds as 'charge-assisted'.

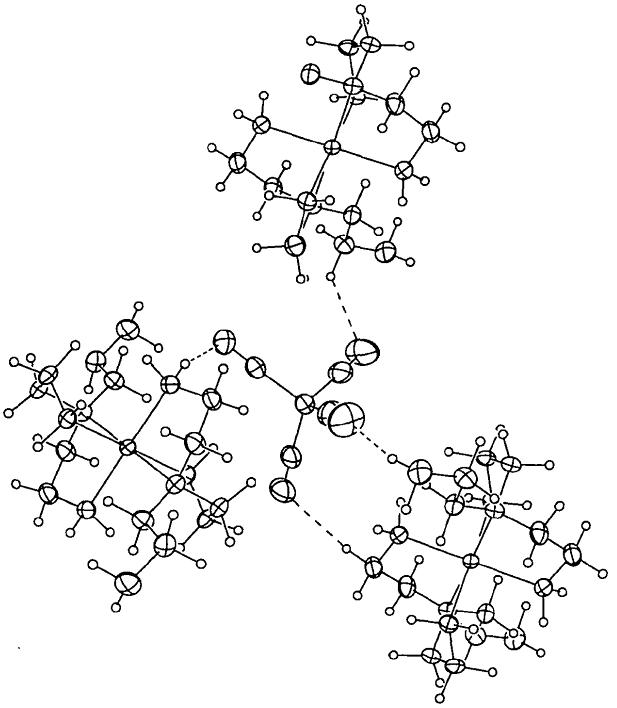


Fig. 2. View of a $[Co(CO)_4]^-$ anion interacting with three neighboring $[Co(tren)_2]^{2+}$ cations *via* X—H···OC—Co hydrogen bonds, shown as dashed lines. Ellipsoids are shown at the 50% probability level.

Experimental

The title complex salt, $[Co(N_4H_{18}C_6)_2][Co(CO)_4]_2$, was prepared under an inert atmosphere of argon, by transferring, *via* standard Schlenk techniques, some of the product of the reaction of $HCo(CO)_4$ with tren in toluene–hexane solution to a flask containing aqueous $CoCl_2$. Slow evaporation of this solution under argon yielded two types of crystals, *i.e.* colorless crystals as the major product, $[(trenH)]^+[Co(CO)_4]^-$ (Brammer & Mareque Rivas, 1998), and pale-orange crystals of (1) as the minor product. The crystal selected for data collection was coated in hydrocarbon oil in an inert-atmosphere drybox and then glued to a glass fiber mounted on a brass pin and placed under the cold stream of the diffractometer.

Crystal data

$[Co(C_6H_{18}N_4)_2][Co(CO)_4]_2$
$M_r = 693.36$
Monoclinic
$P2_1/n$
$a = 9.8829\,(1)$ Å
$b = 12.3755\,(1)$ Å
$c = 12.0482\,(1)$ Å
$\beta = 95.869\,(1)°$
$V = 1465.84\,(2)$ Å^3
$Z = 2$
$D_x = 1.571$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 7893 reflections
$\theta = 2.37–29.88°$
$\mu = 1.733$ mm^{-1}
$T = 208\,(2)$ K
Irregular
0.48 × 0.33 × 0.25 mm
Orange

Data collection

Siemens SMART diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1995)
$T_{min} = 0.554$, $T_{max} = 0.648$
26 148 measured reflections
3972 independent reflections

3243 reflections with $I > 2\sigma(F^2)$
$R_{int} = 0.046$
$\theta_{max} = 29.88°$
$h = -13 \rightarrow 13$
$k = -16 \rightarrow 16$
$l = -16 \rightarrow 16$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.078$
$S = 1.019$
3972 reflections
204 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0445P)^2 + 0.3408P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.010$
$\Delta\rho_{max} = 0.41$ e Å^{-3}
$\Delta\rho_{min} = -0.37$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Co1—N3	2.1800 (13)	Co2—C1	1.769 (2)
Co1—N2	2.1878 (12)	C1—O1	1.152 (3)
Co1—N1	2.2206 (12)	C2—O2	1.152 (3)
Co2—C3	1.757 (2)	C3—O3	1.152 (3)
Co2—C4	1.762 (2)	C4—O4	1.149 (2)
Co2—C2	1.765 (2)		
N3—Co1—N2	94.47 (5)	C4—Co2—C2	110.20 (11)
N3—Co1—N1	80.47 (5)	C3—Co2—C1	103.76 (9)
N2—Co1—N1	79.29 (5)	C4—Co2—C1	108.01 (10)
C3—Co2—C4	112.91 (9)	C2—Co2—C1	113.91 (13)
C3—Co2—C2	107.99 (10)		

Table 2. *Hydrogen-bonding geometry (Å, °; D···A < 2.6 Å and D—H···A > 110°) with D—H distances corrected to standard neutron values*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*	H···*A*—*C*
C42^{i}—H42B^{i}···O1	1.08	2.587	3.447 (3)	136.0	117.9
N4^{ii}—H4B^{ii}···O2	1.01	2.233	3.232 (3)	169.6	155.2
N3^{iii}—H3A^{iii}···O3	1.01	2.280	3.261 (2)	163.2	105.4
C32^{iv}—H32B^{iv}···O4	1.08	2.543	3.460 (3)	142.2	117.8
N2^{i}—H2A^{i}···N4	1.01	2.377	3.242 (2)	142.9	–
N3^{v}—H3B^{v}···N4	1.01	2.201	3.119 (2)	150.4	–

Symmetry codes: (i) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iii) $1 - x, -y, -z$; (iv) $\frac{1}{2} + x, -\frac{1}{2} - y, \frac{1}{2} + z$; (v) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

Disorder in one of the ethylene bridges of the tren ligand was modeled successfully in terms of an 81:19 occupancy of the major and minor components. The empirical absorption correction was based upon symmetry equivalent and repeated intensity measurements using *SADABS* (Sheldrick, 1995), which is based upon the method of Blessing (1995).

Data collection: *SMART* (Siemens, 1994*b*). Cell refinement: *SAINT* (Siemens, 1994*b*). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Siemens, 1994*a*). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1108). Services for accessing these data are described at the back of the journal.

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[3-(*tert*-Butoxycarbonylamino)-4-pyridyl]-trimethyltin(IV), a Tetraorganotin Compound Containing an Unexpected Intramolecular Sn···O Interaction

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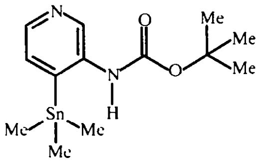
Abstract

The configuration about the Sn centre in the title compound, [Sn(CH$_3$)$_3$(C$_{10}$H$_{13}$N$_2$O$_2$)], is intermediate between tetrahedral and trigonal bipyramidal. A weak intramolecular Sn···O(carbonyl) interaction of 3.070 (3) Å gives rise to an intramolecular six-membered chelate ring, formed through the carbonyl O atom; this is a unique feature of tetraorganotin compounds. The title compound was prepared by consecutive reaction of 3-(*tert*-butoxycarbonylamino)pyridine with *n*-butyllithium and trimethyltin chloride.

Comment

Our approach to the synthesis of streptonigrin (Godard *et al.*, 1993) and related compounds (Molina *et al.*, 1994) employed, among other methods, the palladium(0)-catalysed cross-coupling of 4-metallated-3-aminopyridine derivatives with appropriate aryl halides. Preparation of one of the starting materials by lithiation of 3-(*tert*-butoxycarbonylamino)pyridine with *n*-butyllithium (Turner, 1983), followed by treatment with trimethyltin chloride, afforded the title compound, (I), which readily crystallized from ethyl acetate–hexane. This compound is markedly less reactive in Stille cross-coupling reactions (Farina, 1996) than the corresponding compound lacking the 3-acylamino substituent. As organotin compounds containing coordinating groups such as a ketone, ester or amine in favourable positions sometimes extend their coordination spheres through intramolecular coordination, this relative stability was tentatively ascribed to an intramolecular Sn···O stabilizing interaction. As good quality crystals were available, a crystal structure determination was performed. The structure reported here confirms the postulated intramolecular interaction between the Sn and carbonyl O atoms, thus explaining the stability of the compound.



(I)

Due to the relatively low Lewis acidity of tin in tetraorganotin compounds, known crystal structures containing pentacoordinated tin are scarce. A search of the April 1997 version of the Cambridge Structural Database (Allen & Kennard, 1993) revealed only a small number containing such Sn···O or Sn···N interactions. Examples were found, however, in which the coordination of tin was increased from four to five (Beak & Lee, 1993; Das, Mun, Wei, Blunden & Mak, 1987; Doidge-Harrison *et al.*, 1991; Fu *et al.*, 1995; Jastrzebski *et al.*, 1991; Jousseaume *et al.*, 1988; Jurkschat *et al.*, 1986; Kayser *et al.*, 1994; Murakami *et al.*, 1995; Pearson *et al.*, 1993; Selvaratnam *et al.*, 1994; Veith *et al.*, 1993), and to six (Das, Mun, Wei & Mak, 1987). Even intermolecular interactions of this type are possible in the solid state (Lorberth *et al.*, 1991).

The effect of additional Sn–ligand interactions on chemical reactivity, affording unique synthetic routes to stable organotin compounds, appears to have been

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