

[Bis(*o*-dimethylaminomethylphenyl)methylsilanol-*N,O*]dibromocobalt(II)

RICARDO F. BAGGIO

División Física del Sólido, Departamento de Física, Comisión Nacional de Energía Atómica, Buenos Aires, Argentina

MARIA T. GARLAND

Departamento de Física, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Santiago de Chile, Chile

JORGE MANZUR

Departamento de Química, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Santiago de Chile, Chile

EVGENIA SPODINE

Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Santiago de Chile, Chile

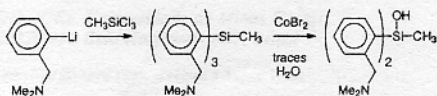
(Received 14 January 1994; accepted 8 August 1994)

Abstract

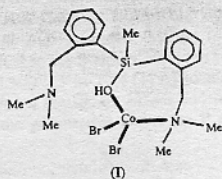
The Co^{II} atom in the title complex, $[\text{CoBr}_2(\text{C}_{19}\text{H}_{28}\text{N}_2\text{O}-\text{Si})]$, has a tetrahedral environment and is coordinated to bis(*o*-dimethylaminomethylphenyl)methylsilanol in a bidentate fashion and to two Br anions.

Comment

Tri(2-picoly)methylsilane has been shown to act as a tripod ligand, binding a metal centre to the three heterocyclic N atoms (Manzur & Musker, 1973). Preparation of similar complexes was attempted with tris(*o*-dimethylaminomethylphenyl)methylsilane. The isolated complex was found to contain the bis(*o*-dimethylaminomethylphenyl)methylsilanol ligand, which results from the hydrolysis reaction of the originally prepared tripod ligand:



The structure of the product, (I), corresponds to a cobalt(II) complex where the first coordination sphere is a tetrahedron formed by two Br ions and an O and N atom provided by the organic lig-



and [Co—Br1 = 2.406 (2), Co—Br2 = 2.385 (2), Co—N2 = 2.100 (8) and Co—O1 = 1.911 (6) Å]. The ligand acts in a bidentate manner and has an intramolecular hydrogen bond between the non-coordinated amine and the silanol O atom [N1...O1 = 2.56 (1) Å]. The

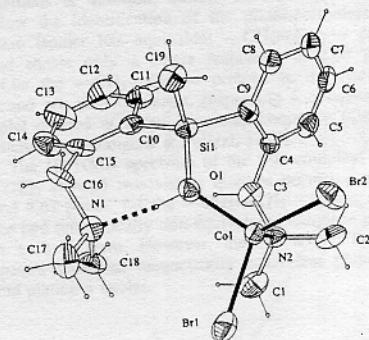


Fig. 1. Displacement ellipsoid plot of the title molecule with ellipsoids drawn at the 50% probability level.

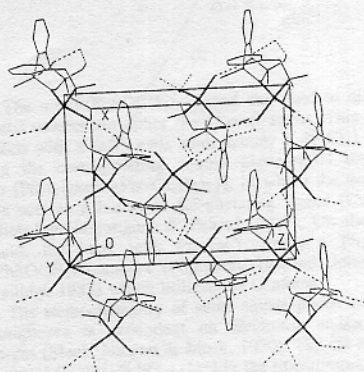


Fig. 2. Packing diagram showing interatomic H...Br contacts. For clarity, only H atoms directly involved in the interactions are included.

dihedral angle between the two phenyl rings of the ligand is 100.7 (5)° and the environment of the Si atom is regular tetrahedral, with Si—O1 = 1.623 (7), Si—C9 = 1.898 (10), Si—C10 = 1.898 (10) and Si—C19 = 1.856 (10) Å (Fig. 1).

The crystal structure is stabilized by three intermolecular hydrogen bonds (Br1...H16a = 2.97, Br1...H18c = 2.94 and Br2...H16b = 2.90 Å).

Experimental

Tris(*o*-dimethylaminomethylphenyl)methylsilane was prepared by the reaction of (*o*-dimethylaminomethyl)phenyllithium with methyltrichlorosilane (1:1 molar ratio) in ether-tetrahydrofuran. The reaction mixture was stirred for 24 h, filtered, and the solution was evaporated until an oily residue was obtained. This residue was dissolved in acetonitrile and a crystalline product was obtained from this solution. The ligand was characterized by ¹H NMR spectroscopy using a CCl₄ solution with an internal standard of tetramethylsilane (TMS). Characteristic peaks were obtained at 7.0–7.6 (multiplet, corresponding to 12H of the phenyl rings), 3.25 (singlet, corresponding to 6H of methylene groups bonded to the phenyl rings), 2.0 (singlet, corresponding to 18H of methyl groups bonded to N atoms) and 0.93 p.p.m. (singlet, corresponding to 3H of methyl group bonded to the Si atom). Anhydrous CoBr₂ was added to a freshly prepared solution of the ligand in acetonitrile. This solution gave blue crystals of the title complex on standing.

Crystal data

[CoBr₂(C₁₉H₂₈N₂OSi)]
M_r = 547.3
 Orthorhombic
*P*2₁2₁
a = 11.8440 (10) Å
b = 12.8710 (10) Å
c = 15.237 (2) Å
V = 2322.7 (5) Å³
Z = 4
D_x = 1.565 Mg m⁻³

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 7.5–12.5°

μ = 4.241 mm⁻¹

T = 293 K

Prismatic

0.24 × 0.16 × 0.14 mm

Deep blue

Data collection

Siemens P3 diffractometer

θ/2θ scans (4.19–

29.3° min⁻¹)

Absorption correction:

ψ scans

T_{min} = 0.380, *T_{max}* =

0.495

2329 measured reflections

2231 independent reflections

1784 observed reflections

[*I* > 4σ(*I*)]

R_w = 0.046

θ_{max} = 22.5°

h = 0 → 12

k = 0 → 13

l = -4 → 13

2 standard reflections

monitored every 98

reflections

intensity decay: none

Refinement

Refinement on *F*

R = 0.039

w*R* = 0.049

S = 0.83

(Δ/σ)_{max} = 0.001

Δρ_{max} = 0.49 e Å⁻³

Δρ_{min} = -0.56 e Å⁻³

Extinction correction: none

1784 reflections
 235 parameters
 Idealized H-atom positions
 riding on host atom
 $w = 1/[\sigma^2(F) + 0.0021F^2]$

Atomic scattering factors
 from *International Tables*
 for *X-ray Crystallography*
 (1992, Vol. C, Tables
 6.1.1.4 and 6.1.1.5)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)*

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Co1	0.0278 (1)	0.0560 (1)	0.5630 (1)	0.0035 (1)
Br1	0.1071 (1)	-0.0715 (1)	0.4654 (1)	0.0068 (1)
Br2	0.1679 (1)	0.1423 (1)	0.6486 (1)	0.0057 (1)
Si1	-0.1622 (2)	0.0314 (2)	0.7067 (2)	0.0037 (1)
N1	-0.1699 (7)	-0.1909 (6)	0.5850 (5)	0.0044 (3)
N2	-0.0694 (6)	0.1608 (6)	0.4892 (5)	0.0042 (3)
O1	-0.0831 (5)	-0.0170 (5)	0.6300 (4)	0.0041 (2)
C1	-0.0931 (10)	0.1145 (9)	0.4018 (7)	0.0066 (5)
C2	-0.0108 (10)	0.2606 (8)	0.4772 (8)	0.0064 (4)
C3	-0.1850 (8)	0.1777 (8)	0.5319 (7)	0.0045 (4)
C4	-0.1799 (8)	0.2322 (7)	0.6178 (6)	0.0037 (3)
C5	-0.1951 (9)	0.3406 (8)	0.6208 (8)	0.0053 (4)
C6	-0.1924 (9)	0.3932 (9)	0.6968 (9)	0.0059 (4)
C7	-0.1732 (10)	0.3444 (9)	0.7761 (9)	0.0063 (5)
C8	-0.1616 (9)	0.2362 (8)	0.7752 (7)	0.0049 (4)
C9	-0.1668 (8)	0.1785 (7)	0.6983 (7)	0.0043 (3)
C10	-0.3120 (8)	-0.0160 (8)	0.6881 (7)	0.0041 (3)
C11	-0.4029 (9)	0.0520 (9)	0.6995 (7)	0.0054 (4)
C12	-0.5150 (9)	0.0195 (12)	0.6878 (9)	0.0078 (6)
C13	-0.5378 (10)	-0.0779 (12)	0.6642 (10)	0.0085 (6)
C14	-0.4502 (9)	-0.1498 (11)	0.6515 (9)	0.0068 (5)
C15	-0.3384 (8)	-0.1213 (8)	0.6662 (7)	0.0047 (4)
C16	-0.2529 (9)	-0.2049 (8)	0.6591 (7)	0.0048 (4)
C17	-0.0906 (10)	-0.2809 (8)	0.5838 (9)	0.0070 (5)
C18	-0.2241 (10)	-0.1801 (9)	0.4981 (7)	0.0061 (4)
C19	-0.1138 (9)	-0.0099 (8)	0.8172 (6)	0.0053 (4)

Table 2. *Selected geometric parameters (\AA , $^\circ$)*

Co1—Br1	2.406 (2)	C3—C4	1.486 (14)
Co1—Br2	2.385 (2)	C4—C5	1.407 (13)
Co1—N2	2.100 (8)	C4—C9	1.416 (14)
Co1—O1	1.911 (6)	C5—C6	1.34 (2)
Si1—O1	1.623 (7)	C6—C7	1.38 (2)
Si1—C9	1.898 (10)	C7—C8	1.40 (2)
Si1—C10	1.898 (10)	C8—C9	1.39 (2)
Si1—C19	1.856 (10)	C10—C11	1.398 (14)
N1—C16	1.507 (14)	C10—C15	1.43 (2)
N1—C17	1.491 (14)	C11—C12	1.40 (2)
N1—C18	1.479 (14)	C12—C13	1.33 (2)
N2—C1	1.485 (14)	C13—C14	1.40 (2)
N2—C2	1.472 (14)	C14—C15	1.39 (2)
N2—C3	1.531 (12)	C15—C16	1.482 (14)
Br1—Co1—Br2	112.6 (1)	N2—C3—C4	113.9 (8)
Br1—Co1—N2	108.7 (2)	C3—C4—C5	119.4 (9)
Br2—Co1—N2	112.1 (2)	C3—C4—C9	122.5 (9)
Br1—Co1—O1	105.3 (2)	C5—C4—C9	118.0 (9)
Br2—Co1—O1	114.5 (2)	C4—C5—C6	121.7 (11)
N2—Co1—O1	103.0 (3)	C5—C6—C7	122.0 (11)
O1—Si1—C9	110.5 (4)	C6—C7—C8	117.4 (11)
O1—Si1—C10	108.0 (4)	C7—C8—C9	122.4 (10)
O1—Si1—C19	106.5 (4)	Si1—C9—C4	123.2 (8)
C9—Si1—C19	111.4 (4)	Si1—C9—C8	118.4 (8)
C10—Si1—C19	110.9 (5)	C4—C9—C8	118.4 (9)
C16—N1—C17	109.4 (5)	Si1—C10—C11	120.0 (8)
C16—N1—C18	109.1 (8)	Si1—C10—C15	123.0 (7)
C17—N1—C18	113.5 (8)	C11—C10—C15	117.0 (9)
Co1—N2—C1	109.6 (8)	C10—C11—C12	121.8 (11)
Co1—N2—C2	109.0 (6)	C11—C12—C13	120.4 (12)
C1—N2—C2	111.6 (6)	C12—C13—C14	120.6 (12)
Co1—N2—C3	109.1 (8)	C13—C14—C15	120.5 (12)
C1—N2—C3	110.8 (6)	C10—C15—C14	119.7 (10)
C2—N2—C3	105.6 (8)	C10—C15—C16	123.7 (9)
Co1—O1—Si1	116.5 (8)	C14—C15—C16	116.6 (10)
	126.4 (4)	N1—C16—C15	114.4 (8)

Data collection: *P3/P4-PC* (Siemens, 1991). Cell refinement: *P3/P4-PC*. Data reduction: *XDISK* in *SHELXTL/PC* (Sheldrick, 1991). Program(s) used to solve structure: *XS* in *SHELXTL/PC*. Program(s) used to refine structure: *XLS* in *SHELXTL/PC*. Molecular graphics: *XP* in *SHELXTL/PC*. Software used to prepare material for publication: *XPUBL* in *SHELXTL/PC*.

The authors would like to thank Fundación Andes for the purchase of the single-crystal diffractometer currently operating at the Universidad de Chile.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, least-squares-planes data and complete geometry have been deposited with the IUCr (Reference: BK1030). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Manzur, J. & Musker, W. K. (1973). *Inorg. Nucl. Chem. Lett.* **9**, 841-843.
- Sheldrick, G. M. (1991). *SHELXTL/PC*. Version 4.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1991). *P3/P4-PC Diffractometer Program*. Version 4.27. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.