

- Bulman, R. A., Jobanputra, N., Kuroda, R., McKinnon, A. & Sadler, P. J. (1987). *Inorg. Chem.* **26**, 2483–2486.
- Fischer, E. & Leuchs, H. (1902). *Chem. Ber.* **35**, 3787–3805.
- Frenz, B. A. (1978). The Enraf–Nonius CAD-4 SDP – A Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution. In *Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi. Delft Univ. Press.
- Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
- Johnson, C. K. (1976). ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Kaitner, B., Kamenar, B., Paulić, N., Raos, N. & Simeon, V. (1987). *J. Coord. Chem.* **15**, 373–381.
- Kramarenko, F. G., Polynova, T. N., Porai-Koshits, M. A., Chalyi, V. P. & Mitrofanova, N. D. (1973). *Zh. Strukt. Khim.* **14**, 1113–1114.
- Narayanan, S., Iyengar, P. L., Ganju, P. L., Shomura, T., Tsuruoka, T., Inouye, S. & Niida, T. (1980). *J. Antibiot.* **33**, 1249–1255.
- Riley, P., Pecoraro, V. L., Carrano, C. J. & Raymond, K. N. (1983). *Inorg. Chem.* **22**, 3096–3103.
- Spek, A. L. (1982). *The EUCLID Package*. In *Computational Crystallography*, edited by D. Sayre. Oxford: Clarendon Press.
- Sysoeva, T. F., Agre, V. M., Trunov, V. K., Dyatlova, N. M. & Barkhanova, N. N. (1984). *Zh. Strukt. Khim.* **25**, 107–113.
- Wieland, Th., Hasan, M. & Pfaender, P. (1968). *Liebigs Ann. Chem.* **717**, 205–214.

Acta Cryst. (1993). **C49**, 1357–1359

Structure of [Di-*tert*-butyl(dimethoxy)-salen]cobalt(II)

WOLFGANG HILLER*

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, D-8046 Garching, Germany

AKIRA NISHINAGA AND TOSHIHIKO TSUTSUI

Department of Applied Chemistry, Osaka Institute of Technology, Ohmiya 5, Asahi-ku, Osaka 535, Japan

ANTON RIEKER

Institut für Organische Chemie der Universität Tübingen, Auf der Morgenstelle 18, D-7400 Tübingen, Germany

(Received 18 May 1992; accepted 28 January 1993)

Abstract

In the monomeric title compound, {6,6'-di-*tert*-butyl-2,2'-[1,2-ethanediylbis(nitrilomethylidyne- κN)]-4,4'-dimethoxy(diphenolato- $\kappa O, O'$)}cobalt(III), the ligand is coordinated *via* two O and two N atoms and the Co atom exhibits an almost planar coordina-

tion sphere with a maximum deviation from planarity of 0.116 (3) Å.

Comment

It has been observed that the formal potential E^0 (Co^{II}/Co^{III}) of Co^{II}(salen) {H₂salen = 2,2'-[1,2-ethanediylbis(nitrilomethylidyne)]diphenol} in dimethylformamide (DMF) is shifted to a more positive value (−408 mV *vs* external F_c/F_c^+) when a *tert*-butyl group is substituted at the 3-position of the aromatic ring of the complex, although from the electronic effects of the *tert*-butyl substituent, a shift in the negative direction would be expected (Nishinaga, Tajima, Speiser, Eichhorn, Ohya-Nishiguchi & Ishizu, 1991). This leads to the assumption that the electronic effects of this bulky substituent are outweighed by steric effects. As a consequence, the planar structure of Co(salen) could become distorted and the coordination of an axial donor ligand (DMF) would be hindered. In order to study these effects we have undertaken X-ray investigations. The crystal structure determination shows only small deviations from planarity in the Co, O1, O2, N1, N2 core. The distances from the plane are −0.011 (2) (Co), 0.115 (2) (O1), −0.110 (2) (O2), −0.111 (3) (N1) and 0.116 (3) Å (N2). Therefore, the *tert*-butyl group should mainly exert a direct steric effect on the coordination of axial donor ligands, thus decreasing the ease of ionization of the Co atom.

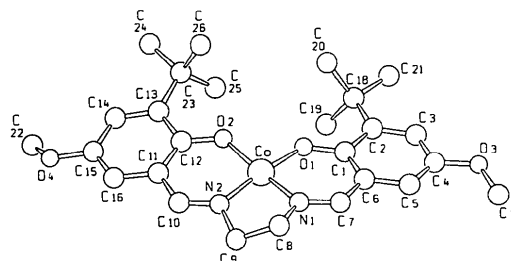


Fig. 1. Plot of the molecule showing the numbering scheme. H atoms have been omitted for clarity.

Experimental

Crystal data

[Co(C₂₆H₃₄N₂O₄)]
 $M_r = 497.50$
 Monoclinic
 $P2_1/n$
 $a = 11.182$ (1) Å
 $b = 17.816$ (1) Å
 $c = 12.137$ (1) Å
 $\beta = 97.437$ (1)°
 $V = 2397.8$ (2) Å³
 $Z = 4$

$D_x = 1.378$ Mg m^{−3}
 Cu $K\alpha$ radiation
 $\lambda = 1.54056$ Å
 Cell parameters from 100 reflections
 $\theta = 18–29^\circ$
 $\mu = 61.464$ mm^{−1}
 $T = 223$ K
 Needle
 $0.4 \times 0.08 \times 0.08$ mm
 Red-brown

Data collection

Enraf-Nonius CAD-4 diffractometer	3235 observed reflections
$\theta/2\theta$ scans	[$I > 3\sigma(I)$]
Absorption correction: empirical (DIFABS; Walker & Stuart, 1983)	$R_{\text{int}} = 0.017$
$T_{\text{min}} = 0.825$, $T_{\text{max}} = 1.327$	$\theta_{\text{max}} = 65^\circ$
4464 measured reflections	$h = 0 \rightarrow 13$
4234 independent reflections	$k = 0 \rightarrow 20$
	$l = -14 \rightarrow 14$
	3 standard reflections
	frequency: 120 min
	intensity variation: none

Refinement

Refinement on F	Extinction correction: Zachariasen (1963)
Final $R = 0.039$	Extinction coefficient: 1.0×10^{-6}
$wR = 0.043$	Atomic scattering factors from <i>International Tables for X-ray Crystallography</i> (1974, Vol. IV, Table 2.2B)
$S = 1.480$	
3235 reflections	
401 parameters	
H-atom positions calculated	
$w = 1/\sigma_F^2$	
$(\Delta/\sigma)_{\text{max}} = 0.01$	
$\Delta\rho_{\text{max}} = 0.295 \text{ e } \text{\AA}^{-3}$	
$\Delta\rho_{\text{min}} = -0.322 \text{ e } \text{\AA}^{-3}$	

All calculations were performed with *MolEN* (Enraf-Nonius, 1990); graphical representation used *SCHAKAL* (Keller, 1988).

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

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

	x	y	z	U_{eq}
Co	0.15442 (5)	0.94231 (3)	0.54267 (4)	0.0185 (2)
O1	0.2714 (2)	1.0010 (1)	0.6229 (2)	0.024 (1)
O2	0.1119 (2)	0.9099 (1)	0.6764 (2)	0.025 (1)
O3	0.6225 (2)	1.1850 (1)	0.4884 (2)	0.029 (1)
O4	-0.3088 (2)	0.7734 (2)	0.7658 (2)	0.039 (1)
N1	0.2063 (2)	0.9652 (2)	0.4084 (2)	0.022 (1)
N2	0.0246 (2)	0.8954 (2)	0.4601 (2)	0.022 (1)
C1	0.3545 (3)	1.0443 (2)	0.5873 (3)	0.020 (2)
C2	0.4353 (3)	1.0865 (2)	0.6661 (3)	0.021 (2)
C3	0.5198 (3)	1.1319 (2)	0.6262 (3)	0.024 (2)
C4	0.5312 (3)	1.1376 (2)	0.5127 (3)	0.023 (2)
C5	0.4561 (3)	1.0987 (2)	0.4368 (3)	0.023 (2)
C6	0.3671 (3)	1.0511 (2)	0.4734 (3)	0.020 (2)
C7	0.2929 (3)	1.0102 (2)	0.3903 (3)	0.023 (2)
C8	0.1441 (3)	0.9224 (2)	0.3136 (3)	0.028 (2)
C9	0.0175 (3)	0.9083 (2)	0.3387 (3)	0.028 (2)
C10	-0.0652 (3)	0.8618 (2)	0.4977 (3)	0.023 (2)
C11	-0.0758 (3)	0.8501 (2)	0.6120 (3)	0.022 (2)
C12	0.0144 (3)	0.8730 (2)	0.6974 (3)	0.021 (2)
C13	-0.0005 (3)	0.8566 (2)	0.8105 (3)	0.023 (2)
C14	-0.1088 (3)	0.8247 (2)	0.8309 (3)	0.026 (2)
C15	-0.2004 (3)	0.8058 (2)	0.7460 (3)	0.027 (2)
C16	-0.1837 (3)	0.8156 (2)	0.6372 (3)	0.024 (2)
C17	0.6303 (3)	1.1957 (2)	0.3723 (3)	0.038 (2)
C18	0.4260 (3)	1.0827 (2)	0.7910 (3)	0.026 (2)
C19	0.3022 (3)	1.1136 (2)	0.8112 (3)	0.037 (2)
C20	0.4406 (3)	1.0012 (2)	0.8327 (3)	0.034 (2)
C21	0.5231 (4)	1.1307 (3)	0.8589 (3)	0.048 (3)
C22	-0.3496 (3)	0.7919 (3)	0.8689 (3)	0.044 (2)
C23	0.1006 (3)	0.8710 (2)	0.9050 (3)	0.025 (2)
C24	0.0677 (4)	0.8458 (2)	1.0186 (3)	0.036 (2)
C25	0.1312 (4)	0.9554 (2)	0.9130 (3)	0.039 (2)
C26	0.2126 (3)	0.8258 (2)	0.8839 (3)	0.037 (2)

Table 2. Geometric parameters (\AA , $^\circ$)

Co—O1	1.851 (2)	C4—C5	1.355 (4)
Co—O2	1.842 (2)	C5—C6	1.422 (5)
Co—N1	1.845 (3)	C6—C7	1.421 (4)
Co—N2	1.853 (3)	C8—C9	1.507 (6)
O1—C1	1.322 (4)	C10—C11	1.423 (5)
O2—C12	1.325 (4)	C11—C12	1.410 (4)
O3—C4	1.386 (5)	C11—C16	1.422 (5)
O3—C17	1.435 (4)	C12—C13	1.435 (5)
O4—C15	1.392 (4)	C13—C14	1.389 (5)
O4—C22	1.425 (6)	C13—C23	1.524 (4)
N1—C7	1.298 (4)	C14—C15	1.397 (4)
N1—C8	1.476 (4)	C15—C16	1.368 (6)
N2—C9	1.483 (4)	C18—C19	1.539 (5)
N2—C10	1.302 (4)	C18—C20	1.540 (5)
C1—C2	1.439 (4)	C18—C21	1.536 (5)
C1—C6	1.414 (4)	C23—C24	1.540 (6)
C2—C3	1.378 (5)	C23—C25	1.543 (5)
C2—C18	1.534 (5)	C23—C26	1.539 (5)
C3—C4	1.404 (5)		
O1—Co—O2	87.7 (1)	C3—C4—C5	120.2 (4)
O1—Co—N1	93.3 (2)	C4—C5—C6	119.5 (3)
O1—Co—N2	172.1 (1)	C1—C6—C5	121.3 (3)
O2—Co—N1	173.9 (1)	C1—C6—C7	121.8 (3)
O2—Co—N2	93.5 (2)	C5—C6—C7	116.9 (3)
N1—Co—N2	86.4 (1)	N1—C7—C6	125.2 (4)
Co—O1—C1	129.6 (2)	N1—C8—C9	106.8 (3)
Co—O2—C12	129.6 (2)	N2—C9—C8	107.2 (3)
C4—O3—C17	115.5 (3)	N2—C10—C11	125.1 (3)
C15—O4—C22	116.3 (3)	C10—C11—C12	122.2 (3)
Co—N1—C7	127.8 (2)	C10—C11—C16	116.9 (3)
Co—N1—C8	113.8 (2)	C12—C11—C16	120.9 (4)
C7—N1—C8	118.3 (3)	O2—C12—C11	122.0 (3)
Co—N2—C9	114.0 (3)	O2—C12—C13	119.0 (3)
Co—N2—C10	127.1 (2)	C11—C12—C13	118.9 (3)
C9—N2—C10	118.4 (3)	C12—C13—C14	117.8 (3)
O1—C1—C2	119.7 (3)	C12—C13—C23	121.3 (3)
O1—C1—C6	122.2 (3)	C14—C13—C23	121.0 (3)
C2—C1—C6	118.1 (3)	C13—C14—C15	122.7 (3)
C1—C2—C3	118.3 (3)	O4—C15—C14	123.0 (3)
C1—C2—C18	121.1 (3)	O4—C15—C16	116.8 (3)
C3—C2—C18	120.6 (3)	C14—C15—C16	120.3 (3)
C2—C3—C4	122.7 (3)	C11—C16—C15	119.2 (3)
O3—C4—C3	114.6 (3)	C2—C18—C19	108.6 (3)
O3—C4—C5	125.2 (4)	C2—C18—C20	110.4 (3)
C2—C18—C21	111.9 (3)	C13—C23—C25	110.4 (3)
C19—C18—C20	110.1 (3)	C13—C23—C26	109.1 (3)
C19—C18—C21	107.6 (3)	C24—C23—C25	107.7 (3)
C20—C18—C21	108.2 (3)	C24—C23—C26	106.9 (3)
C13—C23—C24	112.7 (3)	C25—C23—C26	110.0 (4)

The compound was synthesized by dropwise addition of a solution of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (1 mmol) in methanol (10 ml) under nitrogen to a stirred and refluxed solution of 6,6'-di-*tert*-butyl-2,2'-[1,2-ethanediylbis(nitrilomethylidene)]-4,4'-dimethoxydiphenol (1 mmol) in methanol (20 ml) and 2-propanol (10 ml) containing sodium hydroxide (2 mmol). The resulting solution was refluxed for a further hour and allowed to stand at room temperature for 3 h to yield red-brown fine needle-like crystals which were recrystallized by slow diffusion of toluene into a concentrated solution of the compound in dichloromethane (91% yield).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71043 (48 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1013]

References

- Enraf–Nonius (1990). *MolEN*. Molecular structure solution package, test version. Enraf–Nonius, Delft, The Netherlands.
- Keller, E. (1988). *SCHAKAL*. A Fortran program for the graphical representation of molecules and crystallographic models. Univ. of Freiburg, Germany.
- Nishinaga, A., Tajima, K., Speiser, B., Eichhorn, E., Ohyanishiguchi, H. & Ishizu, K. (1991). *Chem. Lett.* pp. 1403–1407.
- Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.
- Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Acta Cryst. (1993). **C49**, 1359–1361

Structure of the Monomethylgallium Derivative of TMTAA (Dibenzotetramethyltetraaza[14]annulene)[†]

N. W. ALCOCK, N. C. BLACKER, W. ERRINGTON AND M. G. H. WALLBRIDGE*

Department of Chemistry, University of Warwick, Coventry CV4 7AL, England

(Received 10 September 1992; accepted 13 January 1993)

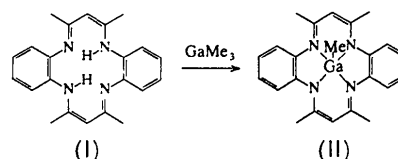
Abstract

The structure consists of a GaCH₃ unit bound symmetrically to the four N atoms of the macrocycle with the metal atom 0.65 (1) Å above the N₄ plane. The four N and C(methyl) atoms form a distorted square-based pyramidal geometry around the Ga atom. The average Ga—N bond distance is 2.016 (5) Å and the Ga—C distance of 1.958 (8) Å is fractionally shorter than the Ga—C distance of 1.967 (2) Å in Ga(CH₃)₃ [Beagley, Schmidling & Steer (1974). *J. Mol. Struct.* **21**, 437–444].

Comment

The reaction of trimethylgallium with the tetraaza macrocycle TMTAA, C₂₂H₂₄N₄ (I), at room temperature results in the loss of one mole of methane and the formation of [(CH₃)₂Ga(C₂₂H₂₃N₄)]. The X-ray crystal structure of this compound shows a Ga(CH₃)₂ group bonded to two N atoms (Alcock, Blacker, Wallbridge & Barker, 1991). Further heating (to 498 K) results in the loss of a second mole of methane and the formation of the title compound (II). The present study was undertaken to determine the structure of this compound and to compare it

with the ethyl aluminium derivative of the same macrocycle (Goedken, Ito & Ito, 1984).



The saddle shape of the free ligand (Goedken, Pluth, Peng & Bursten, 1976) is retained in the metal complex (Fig. 1), with the Ga atom replacing the two H atoms of the two NH groups in the ligand. The metal atom is coordinated essentially symmetrically to the four planar N atoms but is located 0.65 (1) Å above the N₄ plane. This is a significant displacement and is greater than the 0.57 Å observed for the related aluminium compound [(C₂H₅)Al(C₂₂H₂₂N₄)]. However, such displacements are not altogether unexpected since they lie within the range 0.23–0.73 Å observed for cobalt(III), iron(III) and manganese(II) complexes of the same macrocycle (Cotton & Czuchajowska, 1990). It is interesting that the delocalization around the CN framework of the free ligand is not significantly affected by the formation of the metal complex, since the average benzenoid C—N bond distance remains 1.404 (8) Å in both the free ligand and the gallium complex. As expected, the four C—N—C angles in the complex are effectively identical, with mean value 124.8 (5)°, whereas in the free ligand two C—N—C angles are 125° with the other two involving the NH groups opening out to 129°.

Overall, the structure of the title compound shows a close resemblance to that of the free ligand and also to the ethylaluminium derivative. The different distances of the metal atom above the N₄ plane (Ga 0.65, Al 0.57 Å) can be understood in terms of the difference in the respective covalent radii (Ga 1.25, Al 1.18 Å) of the two trivalent metal ions (Alcock, 1990).

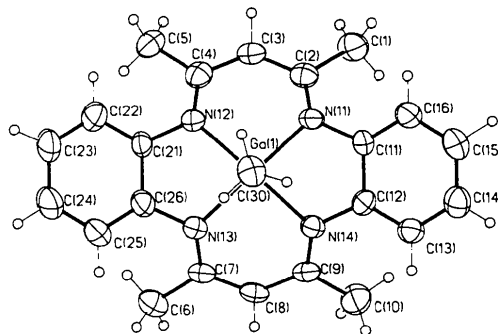


Fig. 1. Face view of (II) showing the atomic numbering with thermal ellipsoids at 50% probability.

[†] TMTAA: 5,14-dihydro-6,8,15,17-tetramethyl-5,9,14,18-tetraazadibenzo[*b,i*]cyclotetradecene.