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# Structures of bis(*N*-*n*-butylsalicylideneiminato)cobalt(II) and bis(*N*-*tert*-butylsalicylideneiminato)cobalt(II) complexes and reactivity towards oxygen and nitric oxide

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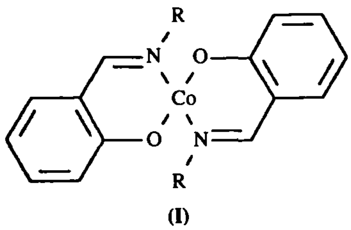
The cobalt(II)-Schiff base complexes [Co(nbsal)$_2$] and [Co(tbsal)$_2$] [nbsal = *N*-*n*-butylsalicylideneiminate and tbsal = *N*-*tert*-butysalicylideneiminate, *o*-OC$_6$H$_4$CH=NR, *R* = Bu$^n$ and Bu$^t$, respectively] both have distorted tetrahedral structures, but the presence of the *tert*-butyl groups in [Co(tbsal)$_2$] causes much greater angular distortion of the coordination tetrahedron. Although [Co(nbsal)$_2$] will react with nitric oxide and oxygen, [Co(tbsal)$_2$] reacts with neither and this appears to be due to the shielding of the cobalt by the *tert*-butyl groups. The reactive complex [Co(nbsal)$_2$] crystallizes in the tetragonal system, $a$ = 14.244, $c$ = 5.395 Å, $Z$ = 2 and space group $P\bar{4}$. The structure was determined by the heavy-atom method, using Mo$K\alpha$ diffractometer data, and refined by full matrix least-squares to $R$ = 0.035 for 777 reflections. The unreactive complex [Co(tbsal)$_2$] crystallizes in the orthorhombic system $Pbc2_1$, $a$ = 10.977, $b$ = 20.037, $c$ = 9.866 Å, $Z$ = 4. The structure was determined as above to $R$ = 0.051 for 1458 reflections.

## Introduction

Cobalt(II) complexes (I) of Schiff bases derived from salicylaldehyde and alkylamines have been reported from their electronic spectra to have tetrahedral configurations in solution in non-donor-solvents (Nishikawa and Yamada, 1964). Irrespective of R the solution spectra are all very similar and different from the spectra of related planar complexes. However, whereas (*I*), *R* = Me, bis(*N*-methylsalicylideneiminato)cobalt(II), forms brown crystals; the other bis(*N*-alkylsalicylideneiminato)cobalt(II) complexes are red. It has been found that the *N*-methyl complex is isomorphous with the corresponding zinc(II) complex which is a dimer with five-coordinate zinc (Orioli *et al.*, 1965). Consequently, it was of interest to determine by single crystal methods whether the red complexes truly contain tetrahedral cobalt(II). It was earlier observed that the cobalt(II) complexes are red whether *R* is an *n*-alkyl group or an $\alpha$-branched alkyl group, and that the *n*-alkyl series are subject to atmospheric oxidation in solutions or as solids whereas the $\alpha$-branched series are indefinitely stable. From the oxidation reaction mixtures tris(*N*-*n*-alkylsalicylideneiminato)cobalt(III) complexes can be isolated (Nishikawa and Yamada, 1964). Cobalt(II) complexes which react with oxygen usually react with nitric oxide, and from this reaction a series of tetragonal pyramidal mononitrosyls (*R* = Me, Et, Bu$^n$, Bz, and Ph) has been isolated (Groombridge et al., 1992). However, the *tert*-butyl derivative, tested as a typical $\alpha$-branched complex, did not react as the solid or in so-



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lution in methanol with nitric oxide paralleling the failure to react with oxygen. The structures of one example of the *n*-alkyl series, bis(*N*-*n*-butylsalicylideneiminato)cobalt(II), [Co(nbsal)$_2$], and one member of the α-branched series, bis(*N*-*tert*-butylsalicylideneiminato)cobalt(II), [Co(tbsal)$_2$], have been determined.

## EXPERIMENTAL

### *Preparation of cobalt(II) complexes*

Bis(*N*-*n*-butylsalicylideneiminato)cobalt(II) was prepared as before by the addition under nitrogen of an excess of *n*-butylamine (2.5 g, 34 mmol) to a solution of bis(salicylaldehydato)cobalt(II) dihydrate (3.0 g, 8.9 mmol) in methanol (80 cm$^3$) containing 2 cm$^3$ of 37% aqueous formaldehyde. The solution was stirred at 60°C for fifteen minutes, allowed to cool and then placed in a refrigerator overnight. The red needles which separated were quickly filtered off and washed with cold methanol (3 cm$^3$) in the air, dried in vacuum and stored under nitrogen (1.35 g, 37%).

The *tert*-butyl analogue was similarly prepared from the same quantities of reactants in methanol (60 cm$^3$) in the air and the red product was recrystallized from ethanol (2.6 g, 72%) to give red crystals.

Analyses for the complexes are given in Table 1. The effective magnetic moments of 4.19 (289 *K*) and 4.23 (289 *K*) for the *n*-butyl- and *tert*-butyl-derivatives are as expected for tetrahedral cobalt(II) complexes.

### *Data collection and processing*

*[Co(nbsal)$_2$]*. A needle crystal of approximate dimensions 0.13 × 0.15 × 0.45 mm obtained as above was mounted on a glass fiber and examined on an Enraf-Nonius CAD4 four-circle diffractometer, using graphite-monochromated Mo*K*α radiation ($\lambda = 0.71073$ Å). The unit cell dimensions were obtained by least-squares refinement of a set of 25 reflections in the $\theta$ range 13 to 15°. Intensity data were collected in a $\omega$-$2\theta$ scan mode from one octant of the reciprocal lattice; $\theta$ range 1 to 26°, $0 \le h \le 17$, $0 \le k \le 17$, $0 \le l \le 6$. After correction for the Lorentz and polarization effects, the data set yielded 1298 independent reflections of which 777 were used ($I > 3\ \sigma(I)$). The 020 reflection, which was monitored hourly throughout the data collection, showed negligible decay (0.1%) in spite of the slight sensitivity of the complex to aerial oxidation. Psi-reflections were not available for the application of an empirical absorption correction. Crystal data are given in Table 2.

**Table 1.** Analytical data (calculated values in parentheses)

| Compound | %C | %H | %N |
|---|---|---|---|
| [Co(C$_6$H$_4$(O)CHNBu$^n$)$_2$] | 64.4 (64.2) | 7.1 (6.9) | 7.0 (6.8) |
| [Co(C$_6$H$_4$(O)CHNBu$^n$)$_2$] | 63.95 (64.2) | 7.0 (6.9) | 7.5 (6.8) |

*[Co(tbsal)$_2$]*. A crystal of approximate dimensions 0.4 × 0.8 × 0.15 mm was examined as above. Intensity data were collected in the $\theta$ range 1 − 24°, and the index range $0 \le h \le 12$, $0 \le k \le 23$, $0 \le l \le 11$. Of the 2304 reflections measured 1819 had non-zero intensity and 1458 had $I > 3\sigma(I)$. Correction was made for the Lorentz and polarization effects and analysis of the standard reflection showed negligible decay of intensity throughout the data collection period. Crystal data are given in Table 2.

### *Structure determination and refinement*

*[Co(nbsal)$_2$]*. Examination of the intensity data revealed that the Laue Group was 4/m ($hkl \neq khl$). The $N(z)$ statistical test gave a distribution line between the centric and noncentric cases. Further examination of the intensity data showed no systematic absences but the hk0 reflections ($h + k$ odd) were systematically weak. The choice of space group was therefore restricted to $P\bar{4}$, $P4$, $P4/m$ or possibly $P4/n$.

The choice for two molecules in the unit cell was made from the knowledge that the approximate atomic volume per atom is 20 Å$^3$, leading to 54 atoms in the cell. Therefore, the Co atom must be sited on a special position in the space group.

The Patterson map was computed and the Co–Co vector was identified and found to be 1/2, 1/2, 0.332. Inspection of the space groups showed that a vector of this type could only occur in space group $P\bar{4}$ although a similar vector occurs in $P4/n$; there are eight general

**Table 2.** Crystal data for [Co(C$_6$H$_4$(O)CHNR)$_2$]

| | *R*=Bu$^n$ | *R*=Bu$^t$ |
|---|---|---|
| Molecular formula | C$_{22}$H$_{28}$CoN$_2$O$_2$ | C$_{22}$H$_{28}$CoN$_2$O$_2$ |
| $M_r$ | 411.41 | 411.41 |
| Crystal system | Tetragonal | Orthorhombic |
| Space group | $P4$ | $Pbc2_1$ (29) [$Pca2_1$] |
| $a$ | 14.244(4) Å | 10.977(2) Å |
| $b$ | 14.244(4) | 20.037(7) |
| $c$ | 5.395(1) | 9.866(3) |
| $V_c$ | 1094.6 Å$^3$ | 2170.0 Å$^3$ |
| $Z$ | 2 | 4 |
| $D_x$ | 1.248 g cm$^{-3}$ | 1.259 g cm$^{-3}$ |
| $F(000)$ | 434 | 868 |
| $\mu$(Mo $K\alpha$) | 7.97 cm$^{-1}$ | 8.04 cm$^{-1}$ |

Table 3. Final positional and thermal parameters for $[Co(C_6H_4(O)CHNBu^n)_2]$ and $B_{eq}$ thermal parameters (Å$^2$)$^a$

| Atom | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| Co | 0.000 | 0.500 | 0.1724(2) | 5.86(2) |
| O | 0.0746(3) | 0.5828(3) | 0.3641(8) | 7.3(1) |
| N | 0.1042(3) | 0.4468(3) | −0.0215(9) | 5.7(1) |
| C1 | 0.1663(4) | 0.5901(4) | 0.360(1) | 5.7(1) |
| C2 | 0.2236(3) | 0.5395(3) | 0.192(1) | 5.0(1) |
| C3 | 0.3216(3) | 0.5524(4) | 0.205(1) | 5.9(1) |
| C4 | 0.3610(4) | 0.6114(4) | 0.372(1) | 7.3(2) |
| C5 | 0.3054(4) | 0.6597(4) | 0.535(1) | 7.2(2) |
| C6 | 0.2110(4) | 0.6500(4) | 0.532(1) | 6.9(2) |
| C7 | 0.1900(4) | 0.4734(4) | 0.015(1) | 5.7(1) |
| C8 | 0.0881(4) | 0.3736(5) | −0.206(1) | 7.8(2) |
| C9 | 0.0438(5) | 0.2881(5) | −0.090(1) | 9.0(2) |
| C10 | 0.1021(7) | 0.2404(6) | 0.101(2) | 12.6(3) |
| C11 | 0.0658(9) | 0.1563(7) | 0.208(3) | 18.9(5) |

$^a$The $B_{eq}$ values are calculated according to the equation $B_{eq} = \frac{4}{3} \Sigma_i \Sigma_j B_{ij} a_i a_j$

positions for this space group, but as there are only four ligands in the unit cell $P\bar{4}$ was accepted as the correct space group and the Co atomic coordinates set at 0, 1/2, 0.166.

Structure factors were calculated on these coordinates and a phased Fourier map calculated. The map revealed the Co atom surrounded by 4 phenyl groups together with the O and N atoms but did not reveal the butyl chain. This result arises because the Co is sited on the two-fold special position and by itself does not phase correctly all the parity groups, resulting in a double image of the structure. One group of 9 atoms was selected and put into the atoms list for refinement.

After four cycles of refinement of structure amplitudes, the $R$ value fell to 0.207 and a difference Fourier revealed the presence of the first two atoms of the butyl chain attached to the N atom. These two atoms were added to the atoms list and further refinement caused $R$ to decrease to 0.149. A second difference Fourier then revealed the last two atoms of the butyl chain. On adding these two atoms to the atom list, further refinement caused $R$ to decrease to 0.089.

Hydrogen atoms were calculated in fixed positions using a C—H distance of 1 Å. When the hydrogens were included $R$ decreased to 0.080. Application of a pseudo empirical absorption correction by DIFABS (Walker and Stuart, 1983) reduced $R$ to 0.075. Anisotropic refinement was applied to all non-hydrogen atoms which caused $R$ to converge at 0.038, $R_w = 0.045$, S = 1.073. Final positional and thermal parameters are given in Table 3, and bond lengths and bond angles in Table 4.

*[Co(tbsal)₂]*. Inspection of the *hk*0, *h*01 and 001 zones revealed the presence of a $b$ glide perpendicular to $a$, and a $c$ glide perpendicular to $b$ leading to the choice of space groups $Pbc2_1$ (29) or $Pbcm$ (57). Intensity statistics favoured the centrosymmetric space group, reflecting the pseudo-symmetric nature of the molecule itself, and would have required the cobalt atom to be sited on a special position. The intensities of the hk0 reflections showed a systematic weakness for those with $(h + k)$ odd. Examination of the Patterson map vectors revealed that it could not be space group $Pbcm$ but could be satisfied by $Pbc2_1$ with the cobalt atom in approximate position 0.25, 0.03, 0.50 where the $x$-coordinate fixes the origin.

Table 4. Bond lengths/Å and bond angles/deg for $[Co(C_6H_4(O)CHNBu^n)_2]$

| Atom 1 | Atom 2 | Distance | Atom 1 | Atom 2 | Distance | Atom 1 | Atom 2 | Distance |
|---|---|---|---|---|---|---|---|---|
| Co | O | 1.894(4) | C1 | C2 | 1.418(8) | C4 | C5 | 1.368(9) |
| Co | N | 1.968(4) | C1 | C6 | 1.411(9) | C5 | C6 | 1.352(9) |
| O | C1 | 1.311(6) | C2 | C3 | 1.410(7) | C8 | C9 | 1.507(10) |
| N | C7 | 1.295(7) | C2 | C7 | 1.422(8) | C9 | C10 | 1.488(12) |
| N | C8 | 1.458(8) | C3 | C4 | 1.353(9) | C10 | C11 | 1.426(15) |

| Atom 1 | Atom 2 | Atom 3 | Angle | Atom 1 | Atom 2 | Atom 3 | Angle | Atom 1 | Atom 2 | Atom 3 | Angle |
|---|---|---|---|---|---|---|---|---|---|---|---|
| O | Co | O | 113.8(2) | O | C1 | C2 | 123.0(5) | C3 | C4 | C5 | 119.9(5) |
| O | Co | N | 96.1(2) | O | C1 | C6 | 119.1(5) | C4 | C5 | C6 | 121.1(6) |
| O | Co | N | 118.3(2) | C2 | C1 | C6 | 117.9(5) | C1 | C6 | C5 | 121.2(6) |
| N | Co | N | 115.7(2) | C1 | C2 | C3 | 118.1(5) | N | C7 | C2 | 127.8(5) |
| Co | O | C1 | 126.8(4) | C1 | C2 | C7 | 124.9(5) | N | C8 | C9 | 111.2(6) |
| Co | N | C7 | 121.2(4) | C3 | C2 | C7 | 117.0(5) | C8 | C9 | C10 | 114.9(6) |
| Co | N | C8 | 121.3(3) | C2 | C3 | C4 | 121.8(5) | C9 | C10 | C11 | 117.4(9) |
| C7 | N | C8 | 117.5(5) | | | | | | | | |

**Table 5.** Final positional and thermal parameters for $[Co(C_6H_4(O)CHNBu^t)_2]$ and $B_{eq}$ thermal parameters (Å$^2$). The $B_{eq}$ values are calculated according to the equation $B_{eq} = \frac{4}{3}\Sigma_i\Sigma_j B_{ij}a_ia_j$

| Atom | $x$ | $y$ | $z$ | $B_{eq}$ | Atom | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|---|---|---|---|---|
| Co | 0.24668(7) | 0.03024(4) | 0.500 | 3.32(2) | C18 | 0.052(1) | 0.0103(7) | 0.721(2) | 13.5(3) |
| O1 | 0.3027(5) | 0.0760(3) | 0.3434(6) | 4.5(1) | C19 | −0.026(2) | 0.1181(6) | 0.714(1) | 25.0(5) |
| O2 | 0.2258(4) | −0.0629(3) | 0.4716(6) | 4.8(1) | C20 | −0.116(1) | 0.040(1) | 0.585(2) | 18.7(6) |
| N1 | 0.0893(4) | 0.0791(2) | 0.5220(6) | 3.3(1) | C21 | 0.2682(6) | −0.1091(4) | 0.5504(9) | 4.1(2) |
| N2 | 0.3700(5) | 0.0241(3) | 0.6486(7) | 3.6(1) | C22 | 0.2375(7) | −0.1757(4) | 0.521(1) | 6.4(3) |
| C1 | 0.0582(6) | 0.1215(3) | 0.4318(9) | 4.0(1) | C23 | 0.2765(9) | −0.2271(4) | 0.601(2) | 7.2(3) |
| C2 | 0.3972(7) | −0.0332(4) | 0.6982(8) | 4.4(2) | C24 | 0.347(1) | −0.2153(4) | 0.714(1) | 7.5(3) |
| C11 | 0.2406(6) | 0.1195(4) | 0.2750(9) | 3.7(1) | C25 | 0.3822(9) | −0.1530(4) | 0.742(1) | 6.2(2) |
| C12 | 0.2905(9) | 0.1467(5) | 0.1550(9) | 5.2(2) | C26 | 0.3455(7) | −0.0985(4) | 0.6646(8) | 4.2(2) |
| C13 | 0.2310(9) | 0.1911(5) | 0.079(1) | 5.8(2) | C27 | 0.4419(7) | 0.0825(3) | 0.6992(8) | 4.1(1) |
| C14 | 0.113(1) | 0.2109(4) | 0.112(1) | 7.0(2) | C28 | 0.377(1) | 0.1440(4) | 0.651(1) | 8.2(3) |
| C15 | 0.0626(9) | 0.1880(4) | 0.227(1) | 5.9(2) | C29 | 0.447(1) | 0.0832(5) | 0.853(1) | 7.8(3) |
| C16 | 0.1231(6) | 0.1430(3) | 0.3132(8) | 3.8(1) | C30 | 0.568(1) | 0.0782(5) | 0.642(1) | 7.8(3) |
| C17 | 0.0029(7) | 0.0646(4) | 0.6356(9) | 4.7(2) | | | | | |

With the addition of two oxygen positions, extracted from its Patterson, as input to the first structure factor/Fourier calculation, $R$ converged at 0.32. Two further cycles of isotropic refinement revealed the remaining atoms of the molecule with $R$ converging to 0.10; hydrogen atoms were included at geometrically calculated positions, $d_H = 1.0$ Å.

In the absence of PSI data for an empirical absorp-

**Table 6.** Bond lengths/Å and bond angles/deg for $[Co(C_6H_4(O)CHNBu^t)_2]$

| Atom 1 | Atom 2 | Distance | Atom 1 | Atom 2 | Distance | Atom 1 | Atom 2 | Distance |
|---|---|---|---|---|---|---|---|---|
| Co | O1 | 1.899(5) | C2 | C26 | 1.464(10) | C21 | C22 | 1.407(11) |
| Co | O2 | 1.901(5) | C11 | C12 | 1.414(12) | C21 | C26 | 1.427(11) |
| Co | N1 | 1.998(5) | C11 | C16 | 1.425(9) | C22 | C23 | 1.37(2) |
| Co | N2 | 1.999(6) | C12 | C13 | 1.336(13) | C23 | C24 | 1.37(2) |
| O1 | C11 | 1.296(9) | C13 | C14 | 1.393(15) | C24 | C25 | 1.337(12) |
| O2 | C21 | 1.296(10) | C14 | C15 | 1.349(15) | C25 | C26 | 1.394(12) |
| N1 | C1 | 1.276(9) | C15 | C16 | 1.405(12) | C27 | C28 | 1.499(12) |
| N1 | C17 | 1.497(10) | C17 | C18 | 1.48(2) | C27 | C29 | 1.522(13) |
| N2 | C2 | 1.283(9) | C17 | C19 | 1.36(2) | C27 | C30 | 1.491(14) |
| N2 | C27 | 1.499(9) | C17 | C20 | 1.49(2) | | | |
| C1 | C16 | 1.437(11) | | | | | | |

| Atom 1 | Atom 2 | Atom 3 | Angle | Atom 1 | Atom 2 | Atom 3 | Angle | Atom 1 | Atom 2 | Atom 3 | Angle |
|---|---|---|---|---|---|---|---|---|---|---|---|
| O1 | Co | O2 | 113.2(2) | C13 | C14 | C15 | 118.9(9) | C22 | C23 | C24 | 121.0(9) |
| O1 | Co | N1 | 97.5(2) | C14 | C15 | C16 | 122.3(9) | C23 | C24 | C25 | 119.7(9) |
| O1 | Co | N2 | 114.0(2) | C1 | C16 | C11 | 124.4(7) | C24 | C25 | C26 | 122(1) |
| O2 | Co | N1 | 113.1(2) | C1 | C16 | C15 | 116.8(7) | C2 | C26 | C21 | 122.9(7) |
| O2 | Co | N2 | 97.4(2) | C11 | C16 | C15 | 118.7(7) | C2 | C26 | C25 | 117.6(7) |
| N1 | Co | N2 | 122.4(2) | N1 | C17 | C18 | 109.7(7) | C21 | C26 | C25 | 119.2(7) |
| C1 | N1 | C17 | 118.8(6) | N1 | C17 | C19 | 114.8(9) | N2 | C27 | C28 | 106.7(7) |
| C2 | N2 | C27 | 116.7(6) | N1 | C17 | C20 | 112(1) | N2 | C27 | C29 | 111.0(7) |
| N1 | C1 | C16 | 129.4(6) | C18 | C17 | C19 | 110(1) | N2 | C27 | C30 | 108.5(7) |
| N2 | C2 | C26 | 128.5(7) | C18 | C17 | C20 | 105(1) | C28 | C27 | C29 | 109.2(8) |
| O1 | C11 | C12 | 119.5(7) | C19 | C17 | C20 | 105(1) | C28 | C27 | C30 | 111.4(8) |
| O1 | C11 | C16 | 124.1(7) | O2 | C21 | C22 | 117.9(8) | C29 | C27 | C30 | 110.1(9) |
| C12 | C11 | C16 | 116.4(7) | O2 | C21 | C26 | 125.5(7) | | | | |
| C11 | C12 | C13 | 122.7(9) | C22 | C21 | C26 | 116.6(8) | | | | |
| C12 | C13 | C14 | 120.8(9) | C21 | C22 | C23 | 121(1) | | | | |

tion correction DIFABS was applied and this reduced $R$ to 0.093, min/max correction 0.65/1.165, average correction 0.98.

Anisotropic refinement, initially Co alone, then all nonhydrogen atoms, caused $R$ to converge at 0.051, $R_w$ = 0.073; $S$ = 1.179. Hydrogen atom positions were recalculated during these last refinement cycles. The weighting scheme was that due to Killean and Lawrence (1969), with $w^{-1} = [\sigma(F^2) + 0.5F + 5.0]$. In the final difference Fourier map, the highest peak was 0.48 electrons. Final positional and thermal parameters are given in Table 5, and bond lengths and bond angles in Table 6.

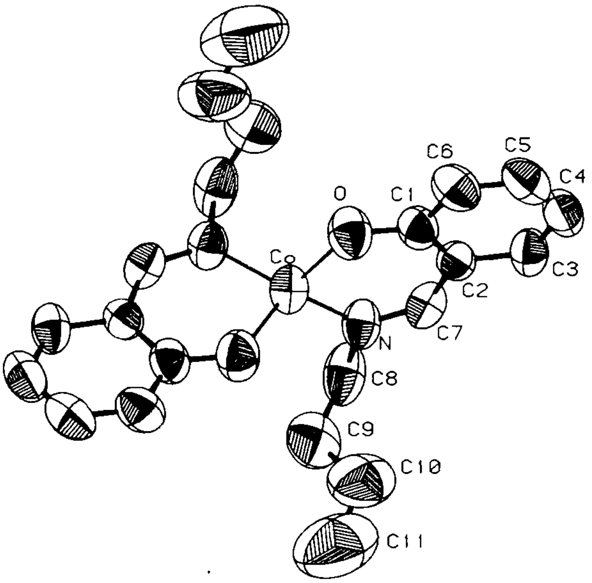

**Fig. 1.** Atom numbering scheme and molecular structure of [Co(nbsal)$_2$].

## Discussion

Both [Co(nbsal)$_2$] and [Co(tbsal)$_2$] have tetrahedral configurations in the solid (Figs. 1 and 2) as predicted from the earlier spectroscopic data, but the bond angles at the cobalt atoms are unequal and very different from the ideal tetrahedral angle (109.5°), particularly in the *tert*-butyl substituted compound. This is partly due to the restriction by the chelate rings which form similar angles at cobalt [Co(nbsal]$_2$, 96.1°; [Co(tbsal)$_2$], 97.1°). However, the *tert*-butyl groups lead to an opening out of the NCoN angle from 115.7° to 122.4° and an increase of the Co—N bond distances from 1.968 to 1.998 Å. The Co—O bond distances are the same within experimental error in both compounds. The O—Co—O angles are similar in both compounds (113.8° and 113.2°), although the O—Co—N angle is smaller in [Co(tbsal)$_2$] (114.0 as opposed to 118.3°).

In [Co(nbsal)$_2$] the *n*-butyl chains lie away from the CoN$_2$ plane leaving regions where NO could attack the cobalt ion to form a mononitrosyl derivative. On the

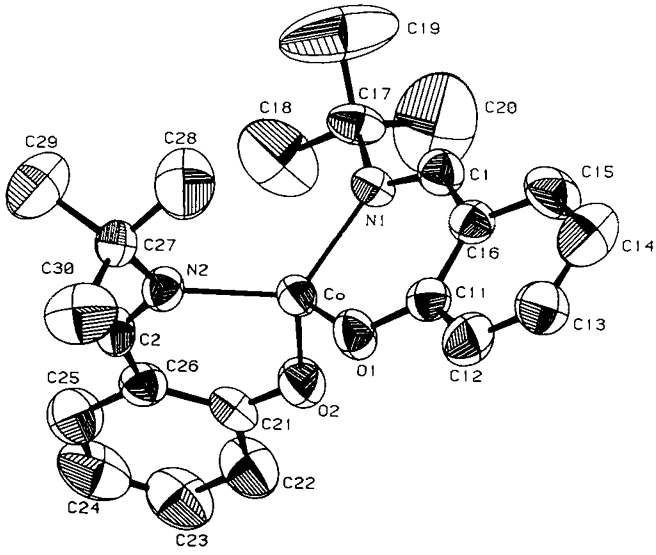

**Fig. 2.** Atom numbering scheme and molecular structure of [Co(tbsal)$_2$].

other hand, in [Co(tbsal)$_2$] the Me groups of the *tert*-butyl substituent block the CoN$_2$ angle as well as lying over the chelate rings and so prevent the attack of NO (and O$_2$). The *tert*-butyl methyl groups also show considerable disorder which manifests itself in very large thermal ellipsoids and a foreshortening of the bond distances, particularly that for C17–C19. There are no short contacts below the normally expected Van der Waals distances in the structure of either cobalt complex.

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