Steric Effect of the Adamantyl Ligand on Crystal Structure† and Dissociation Rates in Organocobalt B_{12} Models

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The synthesis and crystal structure analyses of two new complexes of the type $[Co(Hdmg)_2(ad)L]$, where Hdmg = monoanion of dimethylglyoxime and ad = adamantyl have been performed, with L = (NH_2Ph) (**1**) or 4-dimethylaminopyridine (**2**). Complex (**1**) crystallizes in the triclinic space group $P\bar{1}$ with $a = 11.196(2)$, $b = 15.616(4)$, $c = 16.129(4)$ Å, $\alpha = 70.28(2)$, $\beta = 83.53(2)$, $\gamma = 79.58(2)°$, $Z = 4$, and $R = 0.054$ for 6 133 independent reflections. Complex (**2**) crystallizes in the monoclinic space group $P2_1/c$ with $a = 9.268(3)$, $b = 15.178(2)$, $c = 20.286(4)$ Å, $\beta = 90.31(2)°$, $Z = 4$, and $R = 0.055$ for 3 595 independent reflections. Both compounds are characterized by long axial Co–N bonds 2.215(4) (**1**) and 2.102(3) Å (**2**) and Co–C bonds 2.159(4) (**1**) and 2.160(4) Å (**2**). The steric effect of the ad ligand is evident in the 'butterfly' bending of the Hdmg ligands toward L. In order to determine how such steric effects could be reflected in the rates of L dissociation and in Co–L distances, log k_1 and Co–L bond lengths in series of the type $[Co(Hdmg)_2R(L)]$ with L = NH_2Ph, 1,5,6-trimethylbenzimidazole, 4-cyanopyridine, or $P(OMe)_3$ and R = Me, Et, Pr^i, or ad were analysed as a function of an electronic parameter for R derived from ^{13}C n.m.r. data in a previous study. This analysis suggests that the steric effect of adamantyl on rates is mainly reflected in the transition state.

An important finding in organocobalt B_{12} model chemistry is that the Co–C bond lengthens[1] and its bond dissociation energy decreases[2] as the bulk of the alkyl group R increases. The longest bonds have been found with the adamantyl (ad) (tricyclo[3.3.1.1^{3,7}]decyl) ligand in the cobaloxime B_{12} model system $[Co(Hdmg)_2(ad)L]$ (Hdmg = dimethylglyoximate, L = neutral ligand).[3,4] Bulky alkyl groups are characterized by having several additional structural effects, such as changes in the direction of the cobalt displacement, d, out of the four-N equatorial mean plane and of the 'butterfly' bending, α, of the $(Hdmg)_2$ system.[5] In contrast, this steric effect has been difficult to identify in solution chemistry, although in a recent study[6] evidence was found that the steric effect of R was possibly dominant. Adamantyl appeared to be relatively bulky by this measure.

A major problem in assessing the solution steric effects of R is the absence of a well defined standard of the electronic effect of R. We have explored a series of methods for expressing this.[7,8] One of the less complex measures of the electronic effect, termed the electronic parameter, EP, was defined as the difference in the ^{13}C n.m.r. shift for the γ-C of pyridine (py) in $[Co(Hdmg)_2R(py)]$ complexes and that in $[Co(Hdmg)_2Me(py)]$.[8] In this report, we assess the utility of the EP term in accounting for changes in the dissociation rate constants, k_1, for reaction (1):[8] and in Co–L bond distances. For this purpose we have restricted the analysis to alkyl groups without strong electron-withdrawing substituents at C_α to focus on situations in which the range in electron-donor properties of R is limited in comparison to the change in the bulk of R.

$$[Co(Hdmg)_2R(L)] + L' \longrightarrow [Co(Hdmg)_2R(L')] + L \quad (1)$$

Experimental

Syntheses.—$[Co(Hdmg)_2(ad)(NH_2Ph)]$ (**1**). The complex $[Co(Hdmg)_2Cl(NH_2Ph)]$ (2.07 g, 4.96 mmol) was suspended in methanol (200 cm^3) and N_2 was blown through the solution. Dissolution of the starting material occurred upon addition of a solution formed by dissolving six pellets of KOH in the minimum volume of water. The solution was then warmed (*ca.* 40 °C) and a few drops of an aqueous $NaBH_4$ solution (0.18 g, 4.74 mmol in 2 cm^3 water) were added, followed by 1-bromoadamantane (4.28 g, 19.8 mmol), and the remaining $NaBH_4$ suspension was added to the flask. Heating and stirring under N_2 were continued for 40 min. After this period the red mixture was poured into water (150 cm^3) in a separatory funnel and extracted with two 60-cm^3 portions of CCl_4. The extracts were washed with water (70 cm^3) and dried over $MgSO_4$. The mixture was filtered and the filtrate concentrated on a rotary evaporator. The desired product separated in 21% yield as red-brown needles. This compound was recrystallized by dissolving 0.32 g in acetone (10 cm^3), followed by the addition of water.

$[Co(Hdmg)_2(ad)(NC_5H_4NMe_2\text{-}4)]$ (**2**). To a suspension containing $[Co(Hdmg)_2(ad)(H_2O)]$ (0.10 g, 0.23 mmol) in CH_2Cl_2 (10 cm^3) was added 4-dimethylaminopyridine (0.030 g, 0.24 mmol) dissolved in the minimum amount of CH_2Cl_2. After stirring the mixture until all the starting material dissolved, light petroleum (b.p. 35—60 °C) (*ca.* 15 cm^3) was added to induce the formation of orange needles of the desired compound, which were collected, washed with light petroleum, and air-dried. Yield 81%. The compound was recrystallized from acetone–water after 16 h at 5 °C. All reagents were from Aldrich and were used as received. Both recrystallized compounds were characterized by *X*-ray structural analysis.

Crystallography.—*Crystal data.* Cell dimensions were determined from Weissenberg and precession photographs and refined on a CAD4 Enraf-Nonius single-crystal diffractometer.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Crystallographic data for compounds (**1**) and (**2**)

Formula	(**1**) $C_{24}H_{36}CoN_5O_4{\cdot}1.1H_2O$	(**2**) $C_{25}H_{39}CoN_6O_4{\cdot}0.5C_3H_6O$
M	537.3	575.7
a/Å	11.196(2)	9.268(3)
b/Å	15.616(4)	15.178(2)
c/Å	16.129(4)	20.286(4)
α/°	70.28(2)	
β/°	83.53(2)	90.31(2)
γ/°	79.58(2)	
D_m/g cm^{-3}	1.37	1.35
D_c/g cm^{-3}	1.36	1.34
Z	4	4
Space group	$P\bar{1}$	$P2_1/c$
μ(Mo-K_α)/ cm^{-1}	6.9	6.4
Crystal dimensions/cm	0.02 × 0.02 × 0.04	0.03 × 0.02 × 0.04
F(000)	1 136	1 208
Maxima 2θ(Mo-K_α)/°	56	56
No. measured reflections	12 965	7 314
No. independent reflections [$I > 3\sigma(I)$]	6 133	3 595
R	0.054	0.055
R'	0.069	0.081

The results are given in Table 1. The intensity data were collected by the ω—2θ scan technique, using graphite-monochromated Mo-K_α radiation (λ = 0.7107 Å). Three standard reflections, measured every 50 min, showed no systematic variation throughout the data collection. Intensities having $I > 3\sigma(I)$ were corrected for Lorentz and polarization factors and for anomalous dispersion, but not for absorption, because of the small size of the crystals and the low value of μ (Table 1).

Solution and refinement of the structures. Both the structures were solved by conventional Patterson and Fourier analyses and refined by full-matrix least-squares methods. In complex (**1**) two water molecules of crystallization were located on the Fourier maps. Another electron-density peak was attributed to an additional water molecule O(53), with an occupancy of 0.2. In the final cycles, the contribution of hydrogen atoms at calculated positions (held constant at B = 5.0 Å^2), except those attached to O(53) which was refined isotropically, as well as the anisotropic thermal parameters for non-hydrogen atoms were included. In one of the two crystallographically independent molecules of (**1**) (molecule A in Table 2), two orientations of the adamantyl group with respect to the equatorial ligand, differing by a rotation of *ca.* 60° around the Co–C bond, were found to have occupancies of 0.7 and 0.3, respectively. The contribution of the carbon atoms of the adamantyl in the lowest-occupancy orientation was held constant (B = 6.0 Å^2), while the contribution of their hydrogen atoms was not included. In complex (**2**) an acetone molecule of crystallization with an occupancy factor of 0.5 was located on the Fourier maps. Owing to the disorder, it was not possible to distinguish the acetone oxygen atom, so that all the Fourier peaks were assigned to carbon species. The contribution of these atoms as well as that of the hydrogen atoms, excluding those of the acetone molecule, was included in the final refinement with B = 15.0 and 5.0 Å^2, respectively. Final R and R' values are given in Table 1. The final weighting scheme[9] was $w = 1/[\sigma(F_o{}^2) + (0.02F_o)^2 + 1.0]$ for both structures, chosen so as to maintain $w(|F_o| - |F_c|)^2$ essentially constant over all ranges of F_o and $(\sin\theta)/\lambda$.

Atomic scattering factors were those given in ref. 10. All the calculations were done by using the computer programs from the Enraf-Nonius SDP package.[11] Final positional parameters for non-hydrogen atoms are given in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Discussion

The ORTEP drawings with the atom numbering schemes for complexes (**1**) and (**2**) are given in Figures 1 and 2, respectively. For (**1**), one of the two crystallographically independent molecules is shown. In both compounds the crystals are built up by discrete [Co(Hdmg)$_2$R(L)] molecules held together by van der Waals forces. In (**1**) the two oxime O atoms of the complex molecules are involved in hydrogen bonds with the water molecules of crystallization. The location of the hydrogen atoms on the Fourier difference map suggests that in one of the two independent molecules of (**1**) the equatorial ligands should be formulated as 2 Hdmg, while in the other it should be formulated as dmg and H$_2$dmg.[12] The bond lengths and angles of the Co(Hdmg)$_2$ unit are quite normal.[12] In both structures, the cobalt atom has a distorted octahedral geometry with the neutral ligand and the alkyl group occupying the axial positions. The four N atoms of the equatorial ligand are coplanar with deviations from their mean plane not larger than ±0.002 Å. The geometrical parameters which characterize the axial fragment L–Co–R in compounds (**1**) and (**2**) are given in Table 3, together with the α and d values. The positive sign of α and d indicates a bending toward the alkyl group and a displacement of Co toward the neutral ligand, respectively. A pronounced bending toward the neutral ligand as well as a displacement of Co toward the alkyl group are found.

The geometry of the co-ordinated adamantyl in both compounds (**1**) and (**2**) is characterized by a lengthening of the C–C distances nearly parallel to the Co–C bond and a shortening of those involving C(9) as well as those of the upper six-membered ring (see Figure 1). This ring is squeezed with an opening of the C–C–C angles. Such deformations, deriving from the strong steric interaction between the rigid Hdmg units and the adamantyl group, have been observed in [Co(Hdmg)$_2$(ad){P(OR)$_3$}],[4] with R = Me or Pr^i, and in [Co(Hdmg)$_2$(ad)(tmbzim)] (tmbzim = 1,5,6-trimethylbenzimidazole)[13] complexes and have been interpreted in terms of the anomeric effect.[14]

Data in Table 4, where complexes with L = NH$_2$Ph and

Table 2. Atomic positional parameters of non-hydrogen atoms with estimated standard deviations (e.s.d.s) in parentheses for complexes (**1**) and (**2**)

(*a*) Complex (**1**)

	Molecule A				Molecule B		
Atom	x	y	z	Atom	x	y	z
Co(1)	0.254 61(6)	−0.081 65(4)	0.218 25(4)	Co(2)	0.076 06(6)	0.387 26(4)	0.248 76(4)
O(11)	0.161 0(4)	−0.206 0(3)	0.375 6(2)	O(12)	−0.118 7(4)	0.508 8(2)	0.301 6(2)
O(21)	0.192 2(3)	−0.044 4(2)	0.040 0(2)	O(22)	0.105 9(4)	0.189 7(2)	0.303 9(2)
O(31)	0.337 8(3)	0.049 3(2)	0.062 1(2)	O(32)	0.255 2(3)	0.264 3(2)	0.188 7(2)
O(41)	0.292 0(4)	−0.104 5(3)	0.396 2(2)	O(42)	0.039 2(4)	0.582 5(2)	0.187 8(2)
N(11)	0.160 5(4)	−0.172 2(3)	0.286 3(3)	N(12)	−0.067 1(4)	0.419 6(3)	0.311 3(3)
N(21)	0.177 3(4)	−0.095 4(3)	0.127 1(3)	N(22)	0.037 2(4)	0.269 1(3)	0.310 5(2)
N(31)	0.340 3(3)	0.013 9(3)	0.150 3(3)	N(32)	0.211 6(3)	0.352 9(3)	0.180 8(2)
N(41)	0.319 5(4)	−0.060 8(3)	0.310 9(3)	N(42)	0.109 3(4)	0.505 6(2)	0.182 1(2)
N(51)	0.102 0(4)	0.027 4(3)	0.227 0(3)	N(52)	−0.037 6(4)	0.401 3(3)	0.139 4(3)
C(11)	0.000 5(5)	−0.261 4(4)	0.290 3(4)	C(12)	−0.242 5(5)	0.368 1(5)	0.410 6(4)
C(21)	0.087 5(4)	−0.196 3(3)	0.245 0(3)	C(22)	−0.124 7(5)	0.354 2(4)	0.360 6(3)
C(31)	0.097 7(4)	−0.151 2(3)	0.149 9(3)	C(32)	−0.061 6(5)	0.263 3(3)	0.361 0(3)
C(41)	0.024 6(5)	−0.167 0(4)	0.085 8(4)	C(42)	−0.105 3(6)	0.175 8(4)	0.413 7(4)
C(51)	0.479 7(5)	0.118 6(3)	0.149 9(4)	C(52)	0.361 5(5)	0.403 8(4)	0.058 4(4)
C(61)	0.400 5(4)	0.047 7(3)	0.194 1(4)	C(62)	0.258 6(4)	0.419 7(3)	0.121 5(3)
C(71)	0.383 4(5)	0.005 9(3)	0.288 8(3)	C(72)	0.198 3(5)	0.509 3(3)	0.122 7(3)
C(81)	0.430 1(6)	0.037 6(4)	0.354 2(4)	C(82)	0.234 5(6)	0.598 0(4)	0.063 3(4)
C(91)	0.407 2(4)	−0.183 5(3)	0.206 0(3)	C(92)	0.185 8(4)	0.382 4(3)	0.352 8(3)
C(101)	0.366 3(7)	−0.279 6(5)	0.231 9(6)	C(102)	0.161 4(6)	0.305 8(4)	0.436 6(4)
C(111)	0.461 1(8)	−0.158 5(6)	0.113 4(6)	C(112)	0.150 4(8)	0.472 3(4)	0.373 3(4)
C(121)	0.499 8(8)	−0.192 1(6)	0.269 6(6)	C(122)	0.315 8(6)	0.374 0(8)	0.325 4(4)
C(131)	0.622 7(8)	−0.266 6(6)	0.255 4(5)	C(132)	0.394 7(6)	0.369 6(9)	0.400 4(5)
C(141)	0.566 7(8)	−0.351 4(6)	0.283 5(5)	C(142)	0.366 8(8)	0.291 7(7)	0.482 2(5)
C(151)	0.479 7(8)	−0.353 8(6)	0.223 8(5)	C(152)	0.238 1(6)	0.306 1(4)	0.511 7(4)
C(161)	0.523 0(7)	−0.322 5(5)	0.130 8(5)	C(162)	0.203 9(7)	0.393 8(5)	0.527 5(4)
C(171)	0.573 7(7)	−0.235 1(6)	0.102 8(5)	C(172)	0.227(1)	0.470 0(5)	0.449 7(5)
C(181)	0.657 9(7)	−0.232 1(5)	0.162 4(6)	C(182)	0.354 2(8)	0.460 6(7)	0.419 4(5)
C(191)	−0.018 4(5)	0.005 2(3)	0.245 5(3)	C(192)	−0.149 5(6)	0.365 0(3)	0.160 0(3)
C(201)	−0.089 0(5)	0.011 9(4)	0.177 7(4)	C(202)	−0.255 5(5)	0.420 7(3)	0.173 1(3)
C(211)	−0.201 7(6)	−0.016 3(4)	0.197 9(5)	C(212)	−0.363 4(5)	0.385 6(4)	0.196 6(4)
C(221)	−0.244 4(6)	−0.047 4(4)	0.281 2(5)	C(222)	−0.365 8(5)	0.294 8(4)	0.207 9(5)
C(231)	−0.178 7(6)	−0.052 6(4)	0.348 7(4)	C(232)	−0.260 7(6)	0.239 8(4)	0.193 8(5)
C(241)	−0.062 7(5)	−0.026 9(4)	0.331 6(4)	C(242)	−0.152 7(5)	0.274 2(4)	0.171 0(4)
O(51)	0.166 2(4)	0.201 5(3)	0.069 8(3)	O(52)	0.089 9(4)	0.380 1(3)	−0.040 0(3)
				O(53)	0.150(2)	0.031(2)	0.459(2)

(*b*) Complex (**2**)

Atom	x	y	z	Atom	x	y	z
Co	0.310 27(6)	0.151 46(4)	0.213 19(3)	C(8)	0.144 9(7)	−0.087 1(4)	0.279 8(3)
O(1)	0.574 0(3)	0.073 9(2)	0.169 8(2)	C(9)	0.401 6(5)	0.183 6(3)	0.308 4(2)
O(2)	0.214 1(4)	0.328 5(2)	0.196 3(2)	C(10)	0.366 6(7)	0.112 0(4)	0.359 3(3)
O(3)	0.039 8(4)	0.225 6(3)	0.250 1(2)	C(11)	0.344 2(6)	0.271 6(4)	0.333 7(3)
O(4)	0.403 6(4)	−0.026 9(2)	0.226 9(2)	C(12)	0.566 7(6)	0.190 6(5)	0.304 2(3)
N(1)	0.492 7(4)	0.148 0(3)	0.173 5(2)	C(13)	0.633 3(6)	0.213 6(5)	0.373 5(3)
N(2)	0.322 0(4)	0.269 9(3)	0.187 2(2)	C(14)	0.593 5(7)	0.142 0(4)	0.420 2(4)
N(3)	0.123 7(4)	0.153 0(3)	0.248 7(2)	C(15)	0.433 7(9)	0.135 2(4)	0.428 3(3)
N(4)	0.295 1(4)	0.031 9(2)	0.235 2(2)	C(16)	0.372 1(7)	0.223 3(5)	0.449 7(3)
N(5)	0.220 4(4)	0.122 9(3)	0.120 2(2)	C(17)	0.411 1(7)	0.293 6(4)	0.402 5(3)
N(6)	0.070 2(5)	0.088 5(3)	−0.074 0(2)	C(18)	0.570 7(7)	0.300 3(4)	0.394 2(3)
C(1)	0.677 2(6)	0.225 6(4)	0.110 5(3)	C(19)	0.111 1(5)	0.171 4(3)	0.094 5(3)
C(2)	0.537 7(5)	0.219 8(3)	0.145 8(2)	C(20)	0.058 7(5)	0.161 6(4)	0.032 4(3)
C(3)	0.434 6(6)	0.292 6(3)	0.153 7(2)	C(21)	0.116 7(5)	0.097 9(3)	−0.010 4(2)
C(4)	0.455 2(8)	0.382 6(4)	0.126 1(3)	C(22)	0.227 8(5)	0.046 3(3)	0.017 2(3)
C(5)	−0.081 9(6)	0.067 1(5)	0.289 7(3)	C(23)	0.274 2(5)	0.061 0(3)	0.079 9(2)
C(6)	0.069 1(5)	0.077 9(3)	0.266 2(2)	C(24)	0.131 9(7)	0.025 9(4)	−0.119 0(3)
C(7)	0.173 1(5)	0.005 4(3)	0.259 4(3)	C(25)	−0.043 8(7)	0.143 5(5)	−0.100 0(3)

different R groups are compared, show that the Co–N axial distance increases by about 0.1 Å on going from the Me to the ad derivative and follows the increase in the σ-donor power of the alkyl group (electronic *trans* influence). These values, ranging from 2.129 to 2.215 Å, should be compared with that of 2.019(2) Å reported[15] for [Co(Hdmg)$_2$Cl(NH$_2$Ph)] and are in agreement with the strong *trans* influence of a σ-bonded alkyl group. The Co–C bond length increase of 0.15 Å on going from the Me to the ad derivative and follows the increase in the bulk of the alkyl group (steric *cis* influence). For alkyl groups such as CH$_2$CMe(CO$_2$Et)$_2$, which do not have a 'symmetric' bulk, distortions other than the Co–C lengthening [namely narrowing of the C–Co–N(axial) angle and widening of the Co–C–C angle] contribute significantly to alleviate the steric strains.[12] This is not the case for the adamantyl derivatives, where these angular distortions are not possible and only

Table 3. Geometry of the N–Co–R axial fragment and α and *d* values for compounds (**1**) and (**2**) *

	(**1**)	(**2**)
Co–N	2.215(4)	2.102(3)
Co–C	2.159(4)	2.160(4)
N–Co–R	177.1(2)	178.8(1)
α/°	−10.8	−10.5
d/Å	−0.065	−0.046
C(9)–C(10)	1.50(2)	1.533(4)
C(10)–C(15)	1.561(7)	1.567(5)
C(14)–C(15)	1.48(3)	1.495(11)
Co–C(9)–C(10)	110(1)	111.0(3)
C(10)–C(9)–C(11)	108(2)	107.9(4)
C(9)–C(10)–C(15)	110.3(8)	110.7(2)
C(10)–C(15)–C(14)	108(1)	107.9(6)
C(13)–C(14)–C(15)	111.1(4)	111.2(4)

* The bond lengths (Å) and angles (°) reported for the adamantyl group are mean values obtained assuming local C_{3v} symmetry. For compound (**1**), mean values for the two crystallographically independent molecules are given for the first five entries; the others refer to the non-disordered adamantyl group (molecule B).

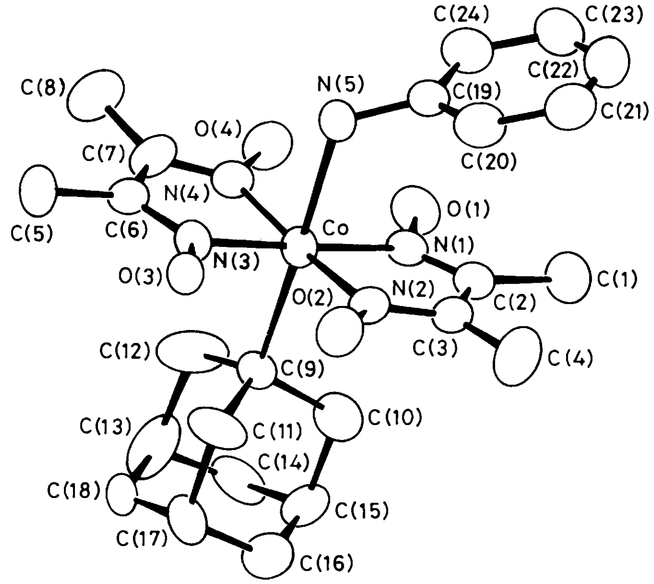

Figure 1. ORTEP drawing of the complex (**1**) with the atom numbering scheme

increases in α and *d* values are observed in addition to the Co–C bond lengthening. No evidence that the σ-donor power of the alkyl group influences the Co–C bond length may be derived from the data in Table 4.

It might be possible to assess the steric effect of R by structural comparisons between the series [Co(Hdmg)$_2$R(NH$_2$Ph)] and [Co(Hdmg)$_2$R(py)]. Relevant geometrical parameters are compared in Table 4, together with the corresponding values of α and *d*. The deformation of the Co(Hdmg)$_2$ moiety is very similar in both series as indicated by the latter parameters, although the change in the crossover point of α and *d*, requiring bulkier R groups for py, suggests that the latter ligand is slightly bulkier than aniline.

Both the Co–C and Co–N distances correlate linearly (Figure 3), see equations (2) and (3). The point for the ad derivative has been omitted from the calculation of equation (3) since the only relevant data are for the NC$_5$H$_4$NMe$_2$-4 derivative, and the *d*(Co–N) value may be different from that of the py analogue. On the contrary, the corresponding Co–C distance has been included in equation (2) since there is evidence[7] that this bond

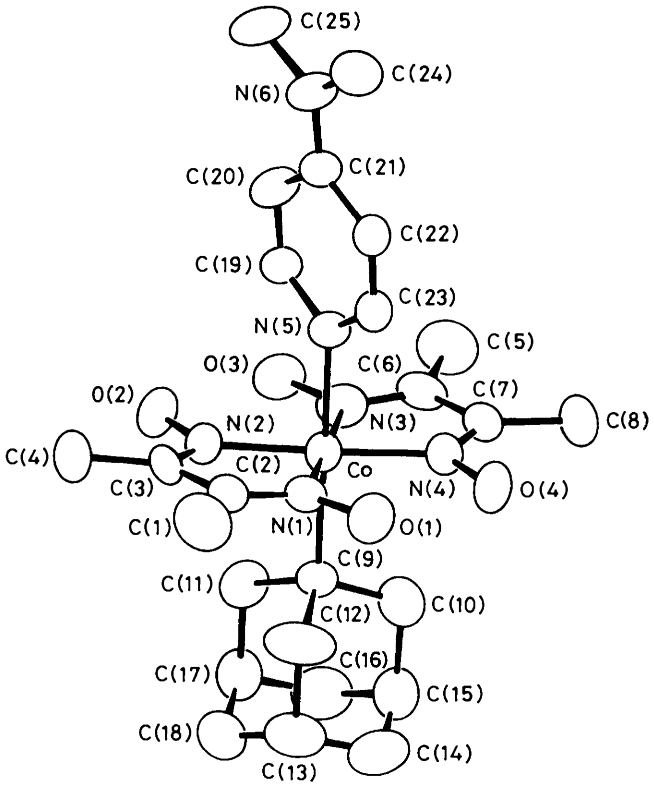

Figure 2. ORTEP drawing of the complex (**2**) with the atom numbering scheme

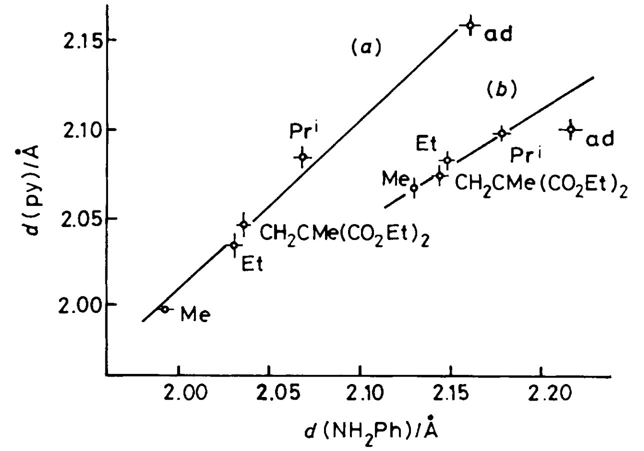

Figure 3. Axial Co–C (*a*) and Co–N (*b*) bond lengths in pyridine derivatives plotted against the corresponding bond lengths in the aniline analogues. The arms of the crosses of each point represent the estimated standard deviations

$$d(\text{Co–C})(\text{py}) = 0.072 + 0.969d(\text{Co–C})(\text{NH}_2\text{Ph}); \quad r = 0.995 \qquad (2)$$

$$d(\text{Co–N})(\text{py}) = 0.676 + 0.654d(\text{Co–N})(\text{NH}_2\text{Ph}); \quad r = 0.994 \qquad (3)$$

Table 4. Structural parameters of [Co(Hdmg)$_2$R(NH$_2$Ph)] complexes. The corresponding values for [Co(Hdmg)$_2$R(py)][a] complexes are given in brackets

R	Co–N/Å	Co–C/Å	N–Co–C/°	Co–C–C/°	Co–N–Ph/°	*d*/Å	α/°
Me[b]	2.129(1)	1.992(2)	178.19(7)	—	118.2(1)	0.04	3.5
	[2.068(3)]	[1.998(5)]	[178.0(2)]	—	—	(0.04)	(3.2)
$CH_2CMe(CO_2Et)_2$[b]	2.143(2)	2.035(2)	170.86(8)	126.8(2)	118.0(1)	−0.01	−3.3
	[2.075(4)]	[2.047(5)]	[176.0(2)]	[130.3(4)]	—	(−0.03)	(−12.3)
Et[c]	2.147(2)	2.030(3)	178.3(1)	117.8(3)	118.1(2)	0.01	2.8
	[2.084(3)]	[2.035(5)]	[177.1(2)]	[117.8(4)]	—	(0.05)	(9.1)
CH_2OMe[c]	2.169(3)	2.013(4)	176.4(2)	119.4(3)	116.6(2)	0.03	2.7
	—	—	—	—	—	—	—
Pr^i[c]	2.177(2)	2.068(3)	178.3(1)	114.2(2)	117.5(2)	−0.02	−5.6
	[2.099(2)]	[2.085(3)]	[174.1(2)]	[114.2(2)]	—	(0.02)	(4.0)
ad[d]	2.215(4)	2.159(4)	177.1(2)	110(1)	118.3(3)	−0.06	−10.8
	[2.102(3)]	[2.160(4)]	[178.8(1)]	[111.0(3)]	—	−0.05	(−10.5)

[a] Ref. 12. [b] Reported in ref. 7. [c] Ref. 7. [d] Present paper, mean values. The neutral ligand for the py derivative is NC$_5$H$_4$NMe$_2$-4.

Table 5. EP values, log k_1 and Co–L distances (Å) in some [Co(Hdmg)$_2$R(L)] complexes

		R				
		Me	Et	Pr^i	ad	Ref.
EP		0	0.12	0.24	0.48	
log k_1	4CN-py	−1.39	−0.02	1.43	—	12
	tmbzim	−2.38	−0.95	0.58	1.61	*a*
	P(OMe)$_3$	−2.38	−1.07	0.36	1.71	4
d(Co–L)	py	2.068	2.081	2.099	2.102	12
	tmbzim	2.060	—	2.097	2.137	13, *b*
	NH$_2$Ph	2.129	2.147	2.177	2.215	7
	P(OMe)$_3$	2.256	—	—	2.313	4

[a] J. P. Charland, E. Zangrando, N. Bresciani Pahor, L. Randaccio, and L. G. Marzilli, to be published. [b] J. P. Charland, W. M. Attia, L. Randaccio, and L. G. Marzilli, to be published.

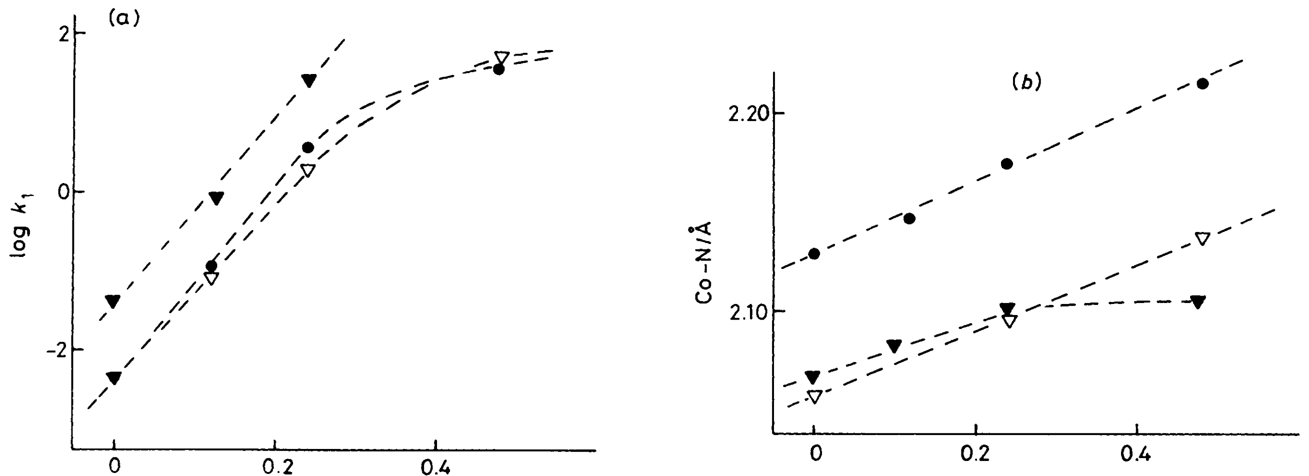

Figure 4. Plots of log *k* (*a*) and Co–L (*b*) against EP relative to data in Table 5, L = (*a*) 4CN-py (▼), tmbzim (●), or P(OMe)$_3$ (▽); (*b*) NH$_2$Ph (●), tmbzim (▽), or py (▼)

length is unaffected by the nature of *trans* N-donor ligands of similar bulk. Indeed, equation (2) further supports the concept that the Co–C bond is little affected by the nature of the *trans* N-donor ligand.

In summary, although relationships between α, *d*, and Co–C bond lengths with the bulk of R are evident, the structural results do not reveal clear evidence for a dependence of Co–L bond length on R bulk.

The values of log k_1 for reaction (1)[8,12] are given in Table 5 for L = 4CN-py, tmbzim, NH$_2$Ph, P(OMe)$_3$, and R = Me, Et, Pr^i, or ad. The axial Co–L bond lengths for the same R groups and L = py, tmbzim, or P(OMe)$_3$ are also reported, together with the EP values for the R groups. These data show that the qualitative trend of log k_1 and Co–L distance is similar, *i.e.* they increase with increasing σ-donor power of R. Plots of log k_1 and Co–L distances against the EP values are reported in Figure 4 and are quite revealing. The Co–L distances exhibit a good linear relationship with EP, for L = NH$_2$Ph or tmbzim. For the py series, the linearity holds for Me, Et, or Pr^i but not for ad. However, we have already stressed that for the latter L is NC$_5$H$_4$NMe$_2$-4. The relationship between log k_1 and EP appears to be linear for R = Me, Et, or Pr^i, but a significant drop of log k_1 with respect to the values required for linearity occurs with ad derivatives. This difference between the changes in log k_1 and Co–L distances as a function of EP suggests that the bulk of ad affects the transition state. The particularly large bulk of the adamantyl group does not allow enough relief of the steric interaction with the equatorial moiety in the [Co(Hdmg)$_2$R] species, as occurs for the other alkyl groups.

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