Structural Study of a New Type of B_{12} Model involving a Non-symmetrical Equatorial Ligand; Aquaethyl[*N,N'*-ethylene(acetylacetonylideneiminato)-(salicylideneiminato)]cobalt(III)†

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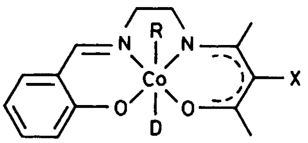
An *X*-ray crystal structure determination has been performed for a new type of B_{12} model involving a non-symmetrical equatorial ligand. Aquaethyl[*N,N'*-ethylene(acetylacetonylideneiminato)-(salicylideneiminato)]cobalt(III) crystallizes in the triclinic space group $P\bar{1}$ with two formula units in a cell having the dimensions a = 9.366(1), b = 11.292(2), c = 8.009(1) Å, α = 99.10(1), β = 102.48(2), and γ = 82.60(1)°. The co-ordination about the cobalt atom is that of a distorted octahedron. The equatorial co-ordination sites are occupied by the N_2O_2 donors from the non-symmetrical Schiff base. A water molecule occupies an axial position with a *trans* σ-bonded ethyl group. Comparison with other types of B_{12} models shows that the present complex is characterized by high values of three structural parameters, *i.e.* the Co–O axial bond length, the dihedral angle between the two halves of the equatorial ligand, and the displacement of the cobalt atom out of the mean plane of co-ordination. These structural features are discussed in relation with other ground-state properties and with the behaviour of the Co–C bond.

Many aspects of the chemistry of cobalamines[1–3] have been investigated through the study of small organocobalt complexes[4] capable of simulating some of the B_{12} reactions. These models allow a systematic change of the metal environment with the goal of obtaining relationships between structural factors and physical or chemical properties.

We have focused our interest on model compounds, [CoL(R)(D)] (R = alkyl) involving symmetrical and non-symmetrical Schiff bases as equatorial ligands (L), D being a neutral ligand (*e.g.* pyridine, water, *etc.*) axially bonded to the metal, and studied the alkyl transfer process between these complexes and tin(IV) compounds.[5–8] From the experimental data, it appears that, in most of the systems investigated, the behaviour of the Co–C bond (*i.e.* cleavage, dinuclear adduct formation, or absence of reaction) correlates to the value of the reduction potential $E_{\frac{1}{2}}$ ($\mathrm{Co^{III}} \longrightarrow \mathrm{Co^{II}}$) in the related complexes. This seems to be indicative of the influence of the electron-donor ability of the equatorial ligand (L) upon the stability of the Co–C bond[9] for a given axial ligand. Surprisingly, the correlation fails for complexes involving the non-symmetrical ligands (L) shown in Figure 1, suggesting that in these cases, factors other than the electronic influence of the equatorial ligand play a prominent part in the behaviour of the Co–C bond. For a literature survey,[9–15] it seems likely that structural and conformational deformations such as distortion of the equatorial ligand and/or steric interactions between the equatorial and the axial ligands can affect the reactivity of the organocobalt complexes. We have therefore undertaken the crystal-structure determination of one of these non-symmetrical complexes, [CoL′(Et)(OH_2)] [L′ = *N,N'*-ethylene(acetylacetonylideneiminate)(salicylideneiminate)]. It may be noted that *X*-ray structural data are restricted to two organometallic B_{12} compounds, namely the coenzyme B_{12}[16] and methylcobalamin.[17] Extensive structural information is available for one class of models, *i.e.* the cobaloximes,[15] but the data are scarce for other types of models. To our knowledge, this is the first report of a structural investigation related to a model compound involving a non-symmetrical equatorial ligand.



X = H, Cl, or Br
R = CH_3 or C_2H_5
D = C_5H_5N or H_2O

Figure 1. Schematic representation of the [CoL(R)(D)] (L = non-symmetrical Schiff base) complexes

Experimental

The complex [CoL′(Et)(OH_2)] was prepared according to the method described previously.[5]

Crystallography.—Crystal data. $C_{16}H_{23}CoN_2O_3$, M = 349.9, triclinic, space group $P\bar{1}$(C_i^1, no. 2), a = 9.366(1), b = 11.292(2), c = 8.009(1) Å, α = 99.10(1), β = 102.48(2), γ = 82.60(1)°, U = 812.7(4) Å^3, Z = 2, D_c = 1.43 g cm^{-3}, F(000) = 368, Mo-K_α radiation, λ = 0.710 73 Å, μ = 10.6 cm^{-1}, 293 K.

Data collection. A red plate-like crystal of dimensions 0.400 × 0.225 × 0.035 mm was centred on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator. The unit-cell dimensions were determined from the setting angles of 25 reflections in the range $12 < \theta < 15°$. A unique data set ($1.5 < \theta < 27°$, $\pm h$, $\pm k$, l) was recorded as previously[18] by the ω–2θ scan technique (scan width 1.20 + 0.35 tan θ, scan speed 1.1—10.1° min^{-1}). The intensities of three standard reflections monitored every 2 h showed no significant variation during data collection. 3 531 Independent reflections were obtained then corrected for Lorentz and polarization effects,[19] 1 685 with $I > 3\sigma(I)$ being considered 'observed' and

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

used in the structure determination. No absorption corrections were made.

Structure determination. The structure was solved by the heavy-atom method using the SHELX 76 system.[20] The Co atom was found by a Patterson map calculation. Subsequent full-matrix least-squares refinement and interpretation of Fourier difference maps enabled all non-hydrogen atoms in the structure to be located; these were refined anisotropically. Hydrogen atoms were located on a Fourier difference map and introduced into the calculations with a constrained geometry (C–H = 0.97 Å) but those bonded to the water oxygen atom had only their bond lengths imposed. All hydrogen atoms were assigned a fixed isotropic thermal parameter $U = 0.07$ Å^2. Neutral-atom scattering factors were used, those for the non-hydrogen atoms being corrected for anomalous dispersion (f', f'').[21] Unit weights were applied and gave satisfactory weight analysis. In the last full-matrix least-squares refinement cycle no shifts were greater than 0.04 times the estimated standard deviation, except for hydrogen water molecule parameters ($<0.3\sigma$), and the final R was 0.032 ($R' = 0.036$). A final Fourier difference map showed a residual electron density of 0.4 e Å^{-3} about the Co atom. All calculations were performed on a VAX-11/730 DEC computer. Atomic co-ordinates are listed in Table 1.

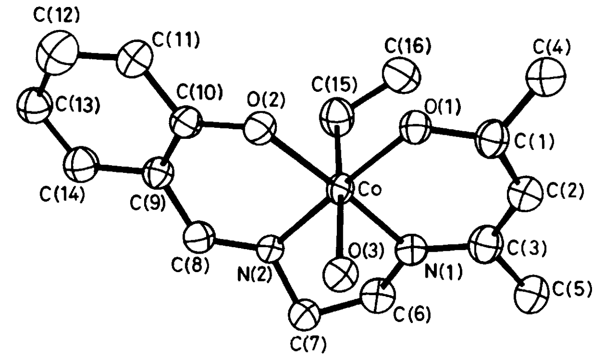

Figure 2. ORTEP plot of the $[CoL'(Et)(OH_2)]$ molecule with the atomic labelling scheme. Hydrogen atoms are omitted for clarity

Results and Discussion

A perspective view of the complex with the atom-numbering scheme is shown in Figure 2. Table 2 lists relevant bond

Table 1. Fractional atomic co-ordinates with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Co	0.431 60(7)	0.213 32(6)	0.458 12(9)
O(1)	0.404 0(3)	0.084 8(3)	0.273 7(4)
C(1)	0.277 2(6)	0.067 1(5)	0.170 8(7)
C(2)	0.149 3(6)	0.137 4(5)	0.179 4(8)
C(3)	0.128 2(6)	0.240 1(5)	0.293 3(8)
C(4)	0.285 9(6)	−0.039 3(5)	0.032 9(7)
C(5)	−0.025 2(6)	0.309 5(5)	0.277 2(8)
N(1)	0.233 9(4)	0.282 6(4)	0.417 8(5)
C(6)	0.211 0(6)	0.396 7(5)	0.530 4(7)
C(7)	0.317 4(5)	0.389 2(5)	0.693 9(7)
N(2)	0.458 1(4)	0.332 5(3)	0.650 2(5)
C(8)	0.580 7(5)	0.366 0(4)	0.744 1(6)
C(9)	0.722 9(5)	0.306 6(4)	0.717 0(6)
C(10)	0.741 0(5)	0.198 6(4)	0.609 0(7)
O(2)	0.630 2(3)	0.142 4(3)	0.512 1(4)
C(11)	0.886 7(6)	0.143 5(5)	0.604 3(8)
C(12)	1.005 7(7)	0.197 8(6)	0.706 2(8)
C(13)	0.986 4(6)	0.305 6(5)	0.812 3(7)
C(14)	0.848 7(6)	0.362 7(5)	0.822 9(7)
C(15)	0.494 7(6)	0.316 4(5)	0.311 9(7)
C(16)	0.434 4(7)	0.302 7(6)	0.125 5(8)
O(3)	0.373 6(3)	0.094 5(3)	0.623 9(4)
H(1O3)	0.325(5)	0.133(4)	0.716(4)
H(2O3)	0.455(3)	0.039(3)	0.699(6)

Table 2. Bond lengths (Å) and angles (°) with e.s.d.s in parentheses

Co environment

Co–O(1)	1.900(3)	Co–N(1)	1.896(4)	Co–O(3)	2.219(4)
Co–O(2)	1.915(3)	Co–N(2)	1.872(4)	Co–C(15)	1.996(6)

O(1)–Co–O(2)	86.0(1)	O(2)–Co–N(1)	176.7(2)	N(1)–Co–O(3)	89.3(2)
O(1)–Co–N(1)	95.8(1)	O(2)–Co–N(2)	93.1(1)	N(1)–Co–C(15)	93.7(2)
O(1)–Co–N(2)	176.0(2)	O(2)–Co–O(3)	88.0(1)	N(2)–Co–O(3)	88.4(2)
O(1)–Co–O(3)	87.7(1)	O(2)–Co–C(15)	89.0(2)	N(2)–Co–C(15)	91.8(2)
O(1)–Co–C(15)	92.1(2)	N(1)–Co–N(2)	84.9(2)	O(3)–Co–C(15)	177.0(2)

Ligand environment

O(1)–C(1)	1.310(6)	C(3)–C(5)	1.535(8)	N(2)–C(8)	1.295(6)	C(11)–C(12)	1.382(8)
C(1)–C(2)	1.358(8)	N(1)–C(6)	1.470(6)	C(8)–C(9)	1.456(7)	C(12)–C(13)	1.385(8)
C(1)–C(4)	1.505(7)	C(6)–C(7)	1.471(7)	C(9)–C(10)	1.393(7)	C(13)–C(14)	1.379(8)
C(2)–C(3)	1.379(8)	C(7)–N(2)	1.477(6)	O(2)–C(10)	1.321(6)	C(14)–C(9)	1.449(7)
C(3)–N(1)	1.323(6)			C(10)–C(11)	1.431(7)		

Co–O(1)–C(1)	123.7(3)	N(1)–C(3)–C(5)	117.6(5)	Co–N(2)–C(8)	127.9(3)	C(9)–C(10)–C(11)	118.7(4)
O(1)–C(1)–C(2)	125.2(5)	Co–N(1)–C(3)	124.6(3)	C(7)–N(2)–C(8)	119.7(4)	O(2)–C(10)–C(11)	117.7(4)
O(1)–C(1)–C(4)	113.1(4)	Co–N(1)–C(6)	112.9(3)	N(2)–C(8)–C(9)	122.3(4)	Co–O(2)–C(10)	124.9(3)
C(2)–C(1)–C(4)	121.6(5)	C(3)–N(1)–C(6)	122.2(4)	C(8)–C(9)–C(10)	123.9(4)	C(10)–C(11)–C(12)	119.7(5)
C(1)–C(2)–C(3)	127.3(5)	N(1)–C(6)–C(7)	107.1(4)	C(8)–C(9)–C(14)	114.9(4)	C(11)–C(12)–C(13)	121.0(5)
C(2)–C(3)–N(1)	123.3(5)	C(6)–C(7)–N(2)	107.2(4)	C(10)–C(9)–C(14)	121.0(4)	C(12)–C(13)–C(14)	122.0(5)
C(2)–C(3)–C(5)	119.1(5)	Co–N(2)–C(7)	112.4(3)	C(9)–C(10)–O(2)	123.5(4)	C(13)–C(14)–C(19)	117.6(5)

C(15)–C(16)	1.469(8)	O(3)–H(1O3)	0.97(4)	Co–O(3)–H(1O3)	117(3)
Co–C(15)–C(16)	119.2(4)	O(3)–H(2O3)	0.97(3)	Co–O(3)–H(2O3)	113(3)
				H(1O3)–O(3)–H(2O3)	109(4)

distances and angles with their estimated standard deviations in parentheses. These data support, definitely, the existence of the non-symmetrical ligand L′ and its ability to complex with cobalt.

In the complex [CoL′(Et)(OH_2)], the cobalt atom has a slightly distorted octahedral co-ordination. The angles around this atom range from 84.9(2) to 95.8(1)°. The four donor atoms, N_2O_2, of the L′ ligand occupy the equatorial positions while the ethyl group and water molecule are axially co-ordinated to the metal. The equatorial N_2O_2 donors are coplanar with a slight tetrahedral deformation [maximum deviation: 0.012(4) Å]. The cobalt atom is displaced by 0.0551(7) Å from the mean co-ordination plane towards the ethyl group. The six-membered ring comprising the cobalt atom and the acetylacetoneimine moiety, Co,O(1),C(1),C(2),C(3),N(1), is planar [maximum deviation of the component atoms: 0.016(6) Å] while more important deviations (up to *ca.* 0.16 Å) from planarity characterize the chelate ring of the salicylideneimine moiety. The two halves of the non-symmetrical ligand are bent towards the ethyl group. This bending is generally described by the dihedral angle (α) between the planes defined by the two ligand residues (not including the metal atom). Considering the mean planes passing through O(2),C(10),C(9),C(8),N(2), on the one hand and O(1),C(1),C(2),C(3),N(1), on the other hand, yields an α value of 11.6°. The ethylene bridge is found to be in a *gauche* conformation. The Co–N bond distance associated with the acetylacteoneimine residue is somewhat longer than that associated with the salicylideneimine residue, while the reverse order is observed for the Co–O bonds. Finally, the overall geometry of the CoL′ unit is significantly distorted from planarity, assuming a flat helical conformation which results mainly from the bending of the two halves of the non-symmetrical ligand towards the ethyl group and, to a much lesser extent, from tetrahedral deformation of the co-ordination plane. The $H_2O–Co–CH_2CH_3$ fragment is characterized by an O(3)–Co–C(15) angle of 177.0(2)° and Co–C(15) and Co–O(3) bond lengths of 1.996(6) and 2.219(4) Å, respectively. As is usually observed, the axial Co–O bond is longer than the equatorial Co–O bonds. The orientation of the ethyl group is such that the C(15)–C(16) bond lies almost on the equatorial Co–O(1) bond. This orientation does not provoke a significant opening of the O(1)–Co–C(15) angle since the observed value of 92.1(2)° is actually smaller than that of the related N(1)–Co–C(15) angle, *i.e.* 93.7(2)°. It may be recalled that in cobaloximes having a σ-bonded CH_2R group (R = alkyl), the $CH_2–CH_3$ bond lies on one of the Co–N equatorial bonds causing an increase of the corresponding N–Co–C angle.[22] As already reported for cobaloximes and related complexes,[13] the bonding to cobalt of the ethyl group significantly alters its geometry. In the title complex, the Co–C(15)–C(16) angle is opened to 119.2(4)° and the C(15)–C(16) distance is shortened to 1.469(8) Å, suggesting a change in hybridization of the carbon bonded to cobalt.

Finally, the structure reveals an intermolecular H-bonding interaction between the oxygen atom O(1) of the acetylacetoneimine moiety of one molecule (*x*, *y*, *z*) and the co-ordinated water molecule of a second molecule (ii; $1 - x$, $-y$, $1 - z$) with the following parameters: $O(3) \cdots O(1^{ii}) = 2.794(3)$, $H(2O3) \cdots O(1^{ii}) = 1.83(3)$ Å, and $O(3)–H(2O3) \cdots O(1^{ii}) = 171(3)°$.

A comparison of some relevant structural parameters observed in the present complex and related [CoL(R)(D)] complexes is presented in Table 3. Inspection of these data shows that [CoL′(Et)(OH_2)] is characterized by high values of three parameters, *i.e.* the Co–O axial bond length, the dihedral angle between the two halves of the equatorial ligand, and the displacement of the cobalt atom out of the co-ordination plane.

Table 3. Relevant geometrical data, distances (Å) and angles (°), for [CoL′(Et)(OH_2)] and other B_{12} models

Compound	*d*(Co–C)	Co–equatorial plane	R–CH_2–Co	C–Co–N_{ax} or C–Co–O_{ax}	*d*(Co–N_{eq})	*d*(Co–O_{eq})	*d*(Co–N_{ax}) or *d*(Co–O_{ax})	α	Ref.
[CoL′(Et)(OH_2)]	1.996(6)	0.055 1(7)	119.2(4)	177.0(2)	1.896(4) 1.872(4)	1.900(3) 1.915(3)	2.219(4)	+11.6	This work
Methylcobalamine	1.99(2)			171.1	2.19(2)		2.18	+15.8	17
[Co(acen)(Me)(py)][a]	1.99(1)	0			1.92	1.92	2.16	+6.9	*b*
[Co(salen)(CH=CH_2)(py)][c]	1.93(2)	0.016	124.6(3)	186.8	1.860(8)	1.878(7)	2.12(1)	+16.8	*d*
[Co(dmg)(Me)(py)][e]	1.998(5)	0.04		178.0(2)	1.897(4)		2.068(3)	+6.3	*f*
[Co(dmg)(Me)(OH_2)]	1.990(5)	0.003		178.0(2)	1.884(3) 1.896(3)		2.058(5)	+3.5	*g*
[Co(dmdauo)(Me)(OH_2)][h]	1.99(4)	0.05		180.7	1.86(4) 1.94(3) 1.92(3) 1.88(3)		2.14(2)	+2.7	*i*
[Co(dedauo)(Me)(OH_2)]PF_6[j]	1.977(4)			178.8(2)	1.881(4) 1.887(4) 1.955(4) 1.907(4)		2.102(3)		25
[Co(acen)(CH=CH_2)(OH_2)]	1.890(1)	0.048	127.2	179.7(4)	1.88(8) 1.89(2)	1.913(7) 1.930(7)	2.221(7)	+11.2	23
[Co(acen)(Ph)(OH_2)]	1.93(2)				1.83	1.91	2.33	−8.9	24
[Co(salen)(Me)(OH_2)]·MeOH	2.02	0.05					2.202(9)		*k*

[a] acen = *N,N′*-Ethylenebis(acetylacetonylideneiminate)(2−). [b] M. Calligaris, G. Nardin, and L. Randaccio. *Inorg. Nucl. Chem, Lett.*, 1972, **8**, 477. [c] salen = *N,N′*-Ethylenebis(salicylideneiminate)(2−). [d] M. Calligaris, G. Nardin, and L. Randaccio, *J. Chem. Soc., Dalton Trans.*, 1972, 1433. [e] dmg = Dimethylglyoximate(2−). [f] N. Bresciani-Pahor, L. Randaccio, E. Zangrando, and P. J. Toscano, *Inorg. Chim. Acta*, 1985, **96**, 193. [g] D. L. McFadden and T. H. McPhail, *J. Chem. Soc., Dalton Trans.*, 1974, 363. [h] dmdauo = 3,9-Dimethyl-4,8-diazaundeca-3,8-diene-2,10-dioximate(1−). [i] S. Bruckner, M. Calligaris, G. Nardin, and L. Randaccio, *Inorg. Chim. Acta*, 1969, **3**, 278. [j] dedauo = 3,9-Diethyl-4,8-diazaundeca-3,8-diene-2,10-dioximate(1−). [k] M. Cesari, C. Neri, G. Perego, E. Perroti, and A. Zazetta, *Chem. Commun.*, 1970, 276; M. Calligaris, G. Nardin, and L. Randaccio, *Coord. Chem. Rev.*, 1972, **7**, 385.

Although each of these values is not the highest within the set of complexes quoted in Table 3, the simultaneous occurrence of three 'abnormal' parameters is noteworthy.

The most interesting feature is the axial Co–O bond since the distances from the cobalt atom to its two axial ligands are expected to reflect the *cis* influence of the equatorial ligand.[14,23,24] As already noted,[25] the Co–C bond length is little influenced by the nature of the equatorial ligand and its variations are expected to reflect mainly modifications of the hybridization state of the carbon bonded to the cobalt and/or steric interactions. Nevertheless, the value of 1.996(6) Å observed for the complex $[CoL'(Et)(OH_2)]$ lies among the largest in Table 3. Much larger variations (from 2.22 to 2.06 Å for the alkylated complexes reported in Table 3) affect the Co–O bond length. From the order of decreasing axial bond lengths, the following order of decreasing *cis*-labilizing influence may be inferred:

$$\text{acen} \approx L' > \text{salen} > \text{dmdauo} > \text{dedauo} < (\text{dmg})_2{}^{*}$$

With the exception of L′, this order is identical to that already reported for aqua and pyridine (py) complexes.[25,26] Interestingly, it parallels the trend suggested by Brown and Flay[27] from thermodynamic data. According to these authors, the order of the *cis*-effect would be: acen > salen > $(dmg)_2$, $(dmg)_2$ causing the strongest axial bonds and acen the weakest.

An important conclusion from the present study is that L′ and acen would display almost identical *cis*-labilizing effects, the axial Co–O bond length being equal to *ca.* 2.22 Å in both cases. This conclusion is unexpected since we have previously shown that the overall donor powers of these two ligands are significantly different. According to Costa *et al.*,[28] the electron-donor abilities of the ligand involved in a series of closely related cobalt complexes may be reflected in the variations of the potential $E_{\frac{1}{2}}(\mathrm{Co^{III}} \longrightarrow \mathrm{Co^{II}})$. For the Co(L)Me series, the values reported, *i.e.* $E_{\frac{1}{2}} = -1.71$ V *vs.* s.c.e. (L = L′) and -1.97 V *vs.* s.c.e.,[6] clearly differentiate the two ligands. This discrepancy between the electrochemical data and the structural and thermodynamic results suggests that, in the [CoL′(R)(D)] complex, the electronic influence of the equatorial ligand is supplemented by steric effects. This would be consistent with the large distortion from planarity which characterizes the CoL′ moiety. A recent theoretical analysis[29] has shown that the organocobalt linkage is particularly susceptible to steric effects.

Our previous work[6,8] has shown that the behaviour of the Co–C bond in the $[CoL(R)(D)]$–$SnMeCl_3$ systems parallels the trend of the redox potential $E_{\frac{1}{2}}(\mathrm{Co^{III}} \longrightarrow \mathrm{Co^{II}})$ with the exception of the complexes involving the non-symmetrical ligands L′. For these complexes, the electron-withdrawing effect of the X substituents exerts the expected influence upon the redox potential but does not significantly alter the behaviour of the Co–C bond.[8] This would be consistent with the hypothesis presented above suggesting that, in non-symmetrical complexes, the behaviour of the Co–C bond would mainly depend on structural and conformational factors. Their prominent contribution would hide a large part of the inductive influence of the substituents. Nevertheless, it should be pointed out that relationships between reactivity and ground-state properties do not take into account the effect of the structure of the transition state. Therefore, only a rough agreement should be expected between the two sets of data. The separation of thermodynamic and 'intrinsic' components of reactivity patterns and the evaluation of their respective importance[30] lies out of the scope of the present paper.

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* Abbreviations used: acen = *N,N*-ethylenebis(acetylacetonylideneiminate)(2−); salen = *N,N′*-ethylenebis(salicylideneiminate)(2−); dmdauo = 3,9-dimethyl-4,8-diazaundeca-3,8-diene-2,10-dioximate(1−); dedauo-3,9-diethyl-4,8-diazaundeca-3,8-diene-2,10-dioximate(1−); dmg = dimethylglyoximate(2−).