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Cobalt(III) Compounds of Carbanions and Their Reactivity.
Part III. Crystal and Molecular Structure of *trans*-3,3,4,4-Tetracyano-2-phenylcyclopentylbis(dimethylglyoximato)imidazolecobalt(III)

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Crystals of the title compound, obtained from tetracyanoethylene and trans-*cinnamylbis(dimethylglyoximato)cobalt(III), were triclinic with* a = *11.869(8),* b = *12.892(8),* c = *10.134(9) Å,* α = *79.90(1),* β = *72.44(2),* γ = *71.75(1)°, space group* $P\bar{1}$, *and Z = 2. The structure was solved by conventional Patterson and Fourier techniques, and refined anisotropically by block-diagonal least-squares methods to a final R of 0.046. The analysis shows the cyclopentyl carbanion ligand to have a* trans *arrangement of substituents. An unusually long Co–C distance of 2.049(7) Å is opposed by an unusually short* trans *Co–N bond to imidazole of 2.007(7) Å. The phenyl substituent of the carbanion ligand appears to be* π*-bonded to a glyoximato moiety. The two short hydrogen bonds between oxygens of opposing glyoximato units are different: one, at 2.455(10) Å, is near the lower limit of observed hydrogen bonds and the other, at 2.518(9) Å, is the longest of any presently known in such 'cobaloxime' structures. The latter is associated with another hydrogen bond between one of the oxygens and the N–H of an imidazole, and with the* π*-bond to the phenyl.*

Introduction

As part of a study of cobalt analogues of vitamin B_{12} coenzymes, the product of the reaction between *trans*-cinnamylbis(dimethylglyoximato)cobalt(III) and tetracyanoethylene was obtained [1] for this X-ray structural determination.

Experimental

Pale yellow crystals were obtained from acetone. Their X-ray powder diffraction pattern was identical with that of the original reaction product, and identical material was obtained from four recrystallisations in good yield (>80%). The only other crystalline species observed in this system was an unstable acetone solvate. And this reverted, on loss of acetone in the solid state to the original crystalline form. Thus the data crystal is confidently regarded as representative of the bulk sample.

The data crystal had approx. dimensions 0.17 × 0.07 × 0.33 mm, and was mounted with the long axis perpendicular to the X-ray beam.

Crystal Data

$C_{26}H_{27}CoN_{10}O_4$, *M* = 602.5, Triclinic, *a* = 11.869(8), *b* = 12.892(8), *c* = 10.134(9) Å, α = 79.90(1), β = 72.44(2), γ = 71.75(1)°. [The Delauney reduced cell is *a* = 13.077, *b* = 14.533, *c* = 10.134 Å, α = 95,21, β = 120.08, γ = 114.75°, and is related to the cell used in the refinement by the transformation matrix

$$\left\{\begin{matrix} 1 & 0 & -1 \\ -1 & 1 & 0 \\ 0 & 0 & 1 \end{matrix}\right\}$$

D_m (flotation) = 1.42 g cm^{-3}, *Z* = 2, D_c = 1.43 g cm^{-3}, *U* = 1398(2) Å^3, F(000) = 624, MoKα radiation, λ = 0.71069 Å; μ(MoKα) = 6.6 cm^{-1}. Space group $P\bar{1}$ [C_i^1, No. 2].

Unit cell data were obtained by a least-squares analysis of the ω-dependence of 70 reflections in layers *hk*0 → *hk*4.

Data were collected on a Stoë Stadi-2 diffractometer with stationary counter and moving crystal, for layers *hk*0 → *hk*12 ($2\theta_{max}$ = 50°). Corrections were applied for Lorentz and polarisation factors, but not for absorption. The total data set, using only reflections with $I/\sigma > 3$, consisted of 2973 unique reflections.

The structure was solved by conventional Patterson and Fourier techniques and refined by block diagonal least-squares, using anisotropic temperature factors for all non-hydrogen atoms, to a final *R* of 0.046.

Carbon and nitrogen atoms of the imidazole moiety were distinguished by the isotropic temperature factors, and their assignment was confirmed by

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TABLE I. Atomic Positions with Estimated Standard Deviations in Parentheses, and Calculated Hydrogen Positions with the Isotropic Thermal Parameters which were used in the Final Refinement.

Atom	*x*/*a*	*y*/*b*	*z*/*c*	
Co	0.2357(1)	0.2182(1)	0.4182(1)	
O(1)	0.0597(6)	0.3352(6)	0.2646(7)	
O(2)	0.2981(6)	−0.0098(5)	0.5087(8)	
O(3)	0.1747(6)	0.4443(5)	0.3292(6)	
O(4)	0.3880(6)	0.1036(5)	0.5951(7)	
N(1)	0.1220(6)	0.2356(6)	0.3133(7)	
N(2)	0.2331(7)	0.0691(6)	0.4350(8)	
N(3)	0.2411(6)	0.3648(5)	0.4014(7)	
N(4)	0.3426(6)	0.2017(6)	0.5297(7)	
N(5)	0.8142(9)	0.0429(10)	0.0722(11)	
N(6)	0.6228(11)	0.3301(10)	0.2823(11)	
N(7)	0.5689(9)	0.0764(7)	−0.1111(9)	
N(8)	0.6291(9)	0.3788(8)	−0.1115(9)	
N(9)	0.0924(6)	0.2457(6)	0.5871(7)	
N(10)	−0.0809(7)	0.3295(7)	0.7253(8)	
C(1)	0.0017(11)	0.1500(12)	0.2306(14)	
C(2)	0.0964(9)	0.1472(9)	0.3027(10)	
C(3)	0.1645(9)	0.0490(8)	0.3712(10)	
C(4)	0.1568(12)	−0.0648(10)	0.3705(14)	
C(5)	0.3174(12)	0.4992(9)	0.4729(12)	
C(6)	0.3087(8)	0.3859(7)	0.4694(9)	
C(7)	0.3709(8)	0.2883(8)	0.5433(9)	
C(8)	0.4578(10)	0.2853(11)	0.6262(11)	
C(9)	0.3751(8)	0.1812(7)	0.2411(8)	
C(10)	0.5029(8)	0.1165(7)	0.2638(9)	
C(11)	0.5973(8)	0.1755(8)	0.1653(9)	
C(12)	0.7203(9)	0.0999(10)	0.1148(10)	
C(13)	0.6114(9)	0.2631(10)	0.2321(10)	
C(14)	0.5336(8)	0.2290(7)	0.0453(8)	
C(15)	0.5511(8)	0.1428(8)	−0.0433(9)	
C(16)	0.5866(8)	0.3145(8)	−0.0434(9)	
C(17)	0.3962(7)	0.2751(7)	0.1296(8)	
C(18)	0.3100(8)	0.3151(7)	0.0353(8)	
C(19)	0.2739(10)	0.4262(9)	−0.0047(10)	
C(20)	0.1939(12)	0.4657(11)	−0.0896(12)	
C(21)	0.1529(12)	0.3963(13)	−0.1319(13)	
C(22)	0.1899(11)	0.2867(12)	−0.0972(12)	
C(23)	0.2693(9)	0.2456(9)	−0.0132(10)	
C(24)	0.0036(8)	0.3377(8)	0.6059(10)	
C(25)	−0.0436(9)	0.2274(9)	0.7876(10)	
C(26)	0.0635(8)	0.1754(7)	0.7013(9)	
H(9)	0.352	0.122	0.200	5.0
H(10)	0.502	0.115	0.359	5.3
H(11)	0.524	0.042	0.243	5.3
H(17)	0.379	0.340	0.174	5.0
H(19)	0.304	0.477	0.028	6.3
H(20)	0.167	0.544	−0.118	8.4
H(21)	0.098	0.425	−0.191	8.4
H(22)	0.160	0.236	−0.131	8.0
H(23)	0.296	0.167	0.014	6.4
H(24)	0.000	0.403	0.540	5.9
H(25)	−0.085	0.198	0.877	6.3
H(26)	0.112	0.101	0.717	5.3
HN(10)	−0.154	0.379	0.767	6.2

TABLE II. Anisotropic Thermal Parameters ($\times 10^5$)[a].

Atom	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
Co	470(1)	413(1)	692(2)	−89(2)	−153(2)	−237(2)
O(1)	679(10)	845(9)	1087(13)	−47(18)	−664(18)	−109(15)
O(2)	981(12)	478(8)	1557(16)	244(18)	−243(22)	−241(16)
O(3)	880(10)	467(7)	944(12)	156(15)	−550(18)	−86(14)
O(4)	892(11)	712(9)	1011(13)	510(17)	−569(20)	67(16)
N(1)	550(10)	745(10)	864(14)	−336(19)	−216(20)	−482(17)
N(2)	702(11)	530(9)	1048(16)	−252(19)	216(22)	−421(17)
N(3)	607(10)	423(8)	709(13)	6(16)	−137(18)	−243(15)
N(4)	604(11)	599(9)	656(13)	130(17)	−201(19)	−93(16)
N(5)	755(14)	1652(20)	1552(23)	520(34)	65(30)	267(28)
N(6)	1759(23)	1620(20)	1607(24)	−388(35)	−1085(38)	−1942(36)
N(7)	1284(17)	748(12)	1210(19)	−677(23)	−104(28)	−502(23)
N(8)	1393(18)	1081(14)	1184(19)	34(26)	73(30)	−1297(27)
N(9)	543(10)	529(9)	743(13)	−192(17)	−32(18)	−290(15)
N(10)	714(12)	720(11)	1037(16)	−303(21)	312(22)	−261(19)
C(1)	1095(21)	1763(25)	1879(31)	−1022(45)	−1019(42)	−1399(38)
C(2)	729(15)	1057(16)	1005(19)	−720(28)	−83(27)	−895(25)
C(3)	755(15)	764(13)	1172(21)	−687(26)	334(28)	−833(23)
C(4)	1368(23)	816(16)	2334(35)	−1111(38)	495(44)	−1416(32)
C(5)	1659(25)	687(14)	1562(26)	−258(30)	−1071(42)	−1085(31)
C(6)	820(15)	648(12)	742(16)	−221(22)	−190(25)	−675(22)
C(7)	665(13)	706(12)	653(15)	−136(22)	−110(23)	−506(21)
C(8)	1023(18)	1461(21)	1054(21)	−73(33)	−1096(33)	−1070(32)
C(9)	607(12)	428(10)	689(15)	−5(19)	−166(22)	−248(18)
C(10)	539(12)	590(11)	812(17)	72(22)	−37(23)	−170(19)
C(11)	526(12)	806(13)	841(17)	−78(24)	−186(24)	−225(21)
C(12)	665(15)	1199(18)	917(19)	342(29)	−68(27)	−278(26)
C(13)	785(16)	1176(17)	973(20)	75(29)	−394(29)	−858(27)
C(14)	526(12)	662(12)	713(16)	−133(21)	−30(22)	−394(19)
C(15)	674(14)	676(12)	772(17)	31(22)	−90(24)	−411(21)
C(16)	692(14)	772(13)	778(17)	−97(23)	−40(24)	−566(22)
C(17)	564(12)	524(10)	676(15)	−186(20)	−135(21)	−323(18)
C(18)	554(12)	646(11)	662(15)	−117(21)	−255(22)	−338(19)
C(19)	1034(18)	753(14)	1028(20)	124(26)	−607(31)	−390(25)
C(20)	1296(22)	1176(20)	1329(26)	331(35)	−1018(39)	−137(34)
C(21)	1087(21)	1995(28)	1231(26)	1(42)	−1137(39)	−437(40)
C(22)	1036(20)	1824(25)	1265(24)	−766(39)	−595(35)	−1256(37)
C(23)	835(16)	1104(16)	949(19)	−466(28)	−405(28)	−836(27)
C(24)	700(14)	595(12)	969(19)	−149(24)	145(26)	−151(21)
C(25)	848(16)	871(14)	847(18)	−74(25)	50(27)	−803(25)
C(26)	751(14)	613(11)	814(17)	−13(22)	−272(25)	−593(21)

[a] The expression for the temperature factor is: $\exp[-(h^2 b_{11} + k^2 b_{22} + l^2 b_{33} + klb_{23} + hlb_{13} + hkb_{12})]$.

the observation of the attached hydrogen atoms in a later difference Fourier map.

Difference Fouriers, based both on the full data set and a limited low-angle data set, showed many of the hydrogen atoms in calculated positions with density up to 0.5eÅ^{-3}. Exceptions were: the methyl group hydrogens, which were 'delocalised' into annuli of electron-density: and the protons of the oximato moieties {O(1)····H····O(3), and O(2)····H····O(4)}, which were but poorly defined – the electron-density in the appropriate regions being not greater than 0.2eÅ^{-3}. Thus no attempt was made to take account of the hydrogens of the glyoximato moieties in the final refinement. Hydrogens attached to methylene and aromatic carbons were generally included, but not refined, in calculated positions at C–H = 0.95 Å. The hydrogen attached to C(9) was, however, inserted in the observed position, which differed significantly from the calculated one. Similarly, the hydrogen attached to N(10) was inserted in the observed position, corresponding to a planar trigonal substituent. Fixed isotropic temperature factors were assigned at values 2.0 greater than the latest refined isotropic values for the atoms to which they are attached.

TABLE III. Bond Lengths (Å) and Angles (°), with Estimated Standard Deviations in Parentheses.

(a) The Co-ordination Sphere on the Metal

(i) Bond Lengths

Co–C(9)	2.049(9)	Co–N(3)	1.888(7)
Co–N(1)	1.896(8)	Co–N(4)	1.882(8)
Co–N(2)	1.909(8)	Co–N(9)	2.007(7)

(ii) Bond Angles

C(9)–Co–N(1)	88.5(3)	N(1)–Co–N(4)	177.4(3)
C(9)–Co–N(2)	86.2(3)	N(2)–Co–N(4)	98.5(3)
C(9)–Co–N(3)	93.3(3)	N(2)–Co–N(9)	89.8(3)
C(9)–Co–N(4)	94.1(3)	N(2)–Co–N(3)	179.1(3)
C(9)–Co–N(9)	174.9(3)	N(3)–Co–N(4)	80.8(3)
N(1)–Co–N(2)	81.3(3)	N(3)–Co–N(9)	90.8(3)
N(1)–Co–N(3)	99.4(3)	N(4)–Co–N(9)	89.5(3)
N(1)–Co–N(9)	87.9(3)		

(b) The Carbanion Ligand

(i) Bond Lengths

C(9)–C(10)	1.55(1)	C(14)–C(16)	1.47(1)
C(9)–C(17)	1.53(1)	C(16)–N(8)	1.13(1)
C(10)–C(11)	1.56(1)	C(14)–C(17)	1.57(1)
C(11)–C(12)	1.48(1)	C(17)–C(18)	1.52(1)
C(12)–N(5)	1.13(2)	C(18)–C(19)	1.38(1)
C(11)–C(13)	1.49(1)	C(18)–C(23)	1.36(1)
C(13)–N(6)	1.14(2)	C(19)–C(20)	1.39(2)
C(11)–C(14)	1.57(1)	C(20)–C(21)	1.32(2)
C(14)–C(15)	1.48(1)	C(21)–C(22)	1.36(2)
C(15)–N(7)	1.12(1)	C(22)–C(23)	1.38(2)
C(9)–H(9)	1.07		

(ii) Bond Angles

C(10)–C(9)–C(17)	106.3(7)	C(11)–C(14)–C(17)	101.5(7)
Co–C(9)–C(10)	115.6(6)	C(15)–C(14)–C(16)	107.7(8)
Co–C(9)–C(17)	117.9(6)	C(15)–C(14)–C(17)	113.5(8)
H(9)–C(9)–Co	103.7	C(16)–C(14)–C(17)	113.2(8)
H(9)–C(9)–C(10)	102.1	C(14)–C(15)–N(7)	177.5(1.0)
H(9)–C(9)–C(17)	110.0	C(14)–C(16)–N(8)	178.9(1.1)
C(9)–C(10)–C(11)	106.9(7)	C(14)–C(17)–C(9)	103.0(7)
C(10)–C(11)–C(12)	113.1(8)	C(14)–C(17)–C(18)	111.8(7)
C(10)–C(11)–C(13)	112.2(8)	C(9)–C(17)–C(18)	117.4(7)
C(10)–C(11)–C(14)	101.5(7)	C(17)–C(18)–C(19)	118.6(8)
C(12)–C(11)–C(13)	108.1(9)	C(17)–C(18)–C(23)	122.4(8)
C(12)–C(11)–C(14)	112.4(8)	C(19)–C(18)–C(23)	119.0(9)
C(13)–C(11)–C(14)	109.4(8)	C(18)–C(19)–C(20)	120.1(1.0)
C(11)–C(12)–N(5)	177.9(1.2)	C(19)–C(20)–C(21)	119.6(1.3)
C(11)–C(13)–N(6)	179.5(1.2)	C(20)–C(21)–C(22)	121.4(1.4)
C(11)–C(14)–C(15)	108.5(8)	C(21)–C(22)–C(23)	120.1(1.3)
C(11)–C(14)–C(16)	112.5(8)	C(22)–C(23)–C(18)	119.9(1.1)

(c) The Imidazole Ligand

(i) Bond Lengths

N(9)–C(24)	1.31(1)	N(10)–C(24)	1.33(1)
N(9)–C(26)	1.37(1)	N(10)–C(25)	1.36(1)
C(25)–C(26)	1.35(1)	N(10)–HN(10)	0.93

(ii) Bond Angles

Co–N(9)–C(24)	125.1(6)	HN(10)–N(10)–C(24)	131.8

(continued on facing page)

TABLE III. *(continued)*

Co–N(9)–C(26)	128.8(6)	HN(10)–N(10)–C(25)	120.9
C(24)–N(9)–C(26)	106.1(8)	C(24)–N(10)–C(25)	107.4(8)
N(9)–C(24)–N(10)	111.1(9)	N(10)–C(25)–C(26)	106.8(9)
		C(25)–C(26)–N(9)	108.7(8)
(d) The Glyoximato Ligands			
(i) Bond Lengths			
N(1)–O(1)	1.36(1)	N(3)–O(3)	1.34(1)
N(2)–O(2)	1.33(1)	N(4)–O(4)	1.35(1)
N(1)–C(2)	1.30(1)	N(3)–C(6)	1.31(1)
N(2)–C(3)	1.29(1)	N(4)–C(7)	1.30(1)
C(1)–C(2)	1.50(2)	C(5)–C(6)	1.50(2)
C(3)–C(4)	1.50(2)	C(7)–C(8)	1.50(2)
C(2)–C(3)	1.46(1)	C(6)–C(7)	1.45(1)
(ii) Bond Angles			
Co–N(1)–O(1)	122.9(6)	Co–N(3)–O(3)	121.5(5)
Co–N(1)–C(2)	116.0(7)	Co–N(3)–C(6)	116.8(6)
Co–N(2)–O(2)	122.2(6)	Co–N(4)–O(4)	121.4(6)
Co–N(2)–C(3)	116.1(7)	Co–N(4)–C(7)	118.0(6)
O(1)–N(1)–C(2)	120.7(8)	O(3)–N(3)–C(6)	121.6(7)
O(2)–N(2)–C(3)	121.8(8)	O(4)–N(4)–C(7)	120.6(8)
N(1)–C(2)–C(1)	121.8(1.0)	N(3)–C(6)–C(5)	123.4(9)
N(1)–C(2)–C(3)	113.4(9)	N(3)–C(6)–C(7)	112.6(8)
C(1)–C(2)–C(3)	124.8(1.0)	C(5)–C(6)–C(7)	124.0(9)
N(2)–C(3)–C(4)	122.1(1.0)	N(4)–C(7)–C(8)	123.1(9)
N(2)–C(3)–C(2)	113.1(9)	N(4)–C(7)–C(6)	111.8(8)
C(2)–C(3)–C(4)	124.7(1.0)	C(6)–C(7)–C(8)	125.1(9)
(e) Hydrogen Bonding			
O(1)---O(3)	2.518(9)	O(3)---N(10)[a]	2.797(10)
O(2)---O(4)	2.455(10)	O(3)---HN(10)[a]	2.28
O(3)---HN(10)[a]–N(10)		114.2°	

[a] Atoms at $-x$, $1-y$, $1-z$.

Anomalous dispersion correctons [2] (both Δf′ and Δf″) were applied for all atoms, and a non-unit weighting scheme was used for the final refinement: $w = 1/\{1 + [(|F_o| - 30)/36]^2\}$.

Fractional co-ordinates for atomic positions, with e.s.d's are given in Table I, together with the positions and isotropic thermal parameters for the hydrogen atoms. Anisotropic thermal parameters for non-hydrogen atoms are in Table II.

The observed molecular geometry and the atom numbering scheme are in Figure 1. Hydrogen atoms attached to carbon are given the same numbers as those carbon atoms, except that the second hydrogen attached to C(10) is labelled H(11) and the hydrogen attached to N(10) is labelled HN-(10).

Atomic scattering factors were taken from ref. 2. Observed and calculated structure factors are listed in a Table available from the Editor.

Results and Discussion

The asymmetric unit consists of one cobalt-containing molecule of the expected type.

Details of the various bond-lengths and angles are given in Table III, and some least-squares planes for parts of the molecule are in Table IV.

The analysis establishes the stereochemistry of the *cyclo*pentyl addition product as *trans*.

The β-carbon of the original [1] *trans*-cinnamyl group is σ-bonded to the cobalt at a distance {Co–C(9) = 2.049(7) Å} which is at the upper limit of presently observed Co–C bonds [3–5]. In contrast, the *trans* bond to a nitrogen of the imidazole {Co–N(9) = 2.007(7) Å} is the shortest of any known Co–N bond-length *trans* to a carbon [3–5]. This 'inversion' of the normally observed Co–C and Co–N bond-lengths has an obvious rationalisation in the bulkiness of the carbanion ligand (see below).

TABLE IV. Equations of Some Least-squares Planes Given in the Form $lX + mY + nZ = d$ (where X, Y and Z are co-ordinates in Å referred to the axes a, b^* and c'). The deviations of the various atoms from these planes are given in square brackets. Angles between some of the planes are listed at the end of the Table.

	l	m	n	d
Plane (1): N(1)–N(4)				
	0.5228	−0.1721	−0.8349	−1.4558
[Co 0.017, C(18) 2.87, C(19) 2.80, C(20) 2.82, C(21) 2.90, C(22) 3.00, C(23) 2.99, See also Figure 2]				
Plane (2): C(9)–(10), C(17)				
	0.2627	0.5860	0.7665	4.7879
[Co 1.35, C(11) 0.02, C(14) −0.68]				
Plane (3): C(10)–(11), C(14)				
	−0.0889	0.8229	0.5612	2.0269
[Co 2.12, C(9) 0.68, C(17) 1.05, C(12) −1.17, C(13) 1.23, C(15) −1.36, C(16) 0.37]				
Plane (4): C(18)–(23)				
	−0.5616	0.1025	0.8210	−1.8985
[C(17) 0.03, C(18) 0.01, C(19) −0.01, C(20) −0.01, C(21) 0.01, C(22) −0.01, C(23) −0.01]				
Plane (5): N(9), C(24), C(26)				
	0.8086	0.3259	0.4899	7.0264
[Co −0.05, N(10) −0.02, C(25) 0]				
Angles between planes (°)				
	(1)–(2)	127.1	(1)–(5)	92.4
	(1)–(3)	131.0	(2)–(3)	27.2
	(1)–(4)	175.4		

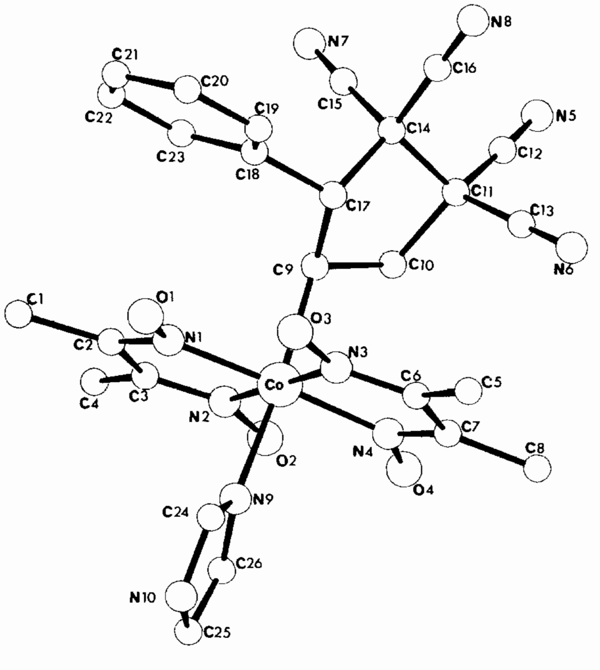

Figure 1. The molecule and the atom labelling scheme. Hydrogens attached to carbons are given the same numbers as the carbon atoms, except that H(11) is the second hydrogen attached to C(10) and HN(10) is attached to N(10).

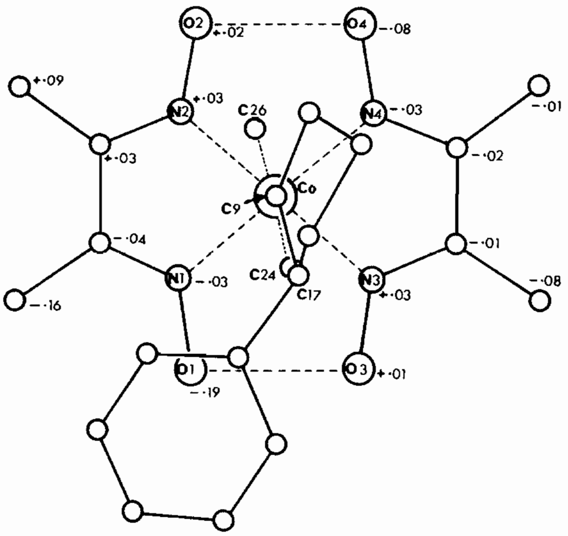

Figure 2. A projection of the molecule on the $[N_4]$ plane {Plane (1) of Table IV}. C(24) and C(26) of the imidazole are shown to give the orientation of this ligand. Heights above and below the plane are shown to illustrate some distortions in the molecule.

For the latter, the cyclopentyl ring appears to have a normal conformation, defined entirely by intramolecular forces. It is puckered in such a way that

TABLE V. Some Inter-atom Close[a] Contacts (Å) that are Probably Affecting Relative Orientations of the Ligands.

(a) Imidazole

Intramolecular		Intermolecular*	
C(24)----N(1)	3.19	C(24)----O(3)$^{\mathrm{I}}$	2.98[b]
N(3)	3.03	H(24)----O(3)$^{\mathrm{I}}$	2.57[b]
H(24)----N(1)	3.13	H(24)$^{\mathrm{I}}$	2.49
N(3)	2.71	C(25)----H(22)$^{\mathrm{II}}$	2.82
O(1)	2.89	H(25)----N(5)$^{\mathrm{III}}$	2.83
O(3)	2.60	C(26)----H(22)$^{\mathrm{II}}$	2.65
C(26)----N(2)	3.08	H(26)----N(5)$^{\mathrm{IV}}$	2.74
N(4)	3.34	N(10)----N(8)$^{\mathrm{III}}$	3.25
H(26)----N(2)	2.82	HN(10)----N(8)$^{\mathrm{III}}$	2.50
N(4)	3.32		
O(2)	2.76		
O(4)	3.14		

(b) Cyclopentyl Ligand

Intramolecular[c]		Intermolecular*	
H(9)----N(1)	2.67	H(9)----N(7)$^{\mathrm{V}}$	2.65
N(2)	2.48	C(10)----O(4)$^{\mathrm{IV}}$	3.03
C(2)	2.83	H(10)----O(2)$^{\mathrm{IV}}$	2.92
C(3)	2.69	O(4)$^{\mathrm{IV}}$	2.73
C(10)----N(2)	3.34	H(11)----O(4)$^{\mathrm{IV}}$	2.46
N(4)	2.95	N(7)$^{\mathrm{V}}$	2.83
O(2)	3.48	N(5)----H(25)$^{\mathrm{VI}}$	2.83
O(4)	3.22	H(26)$^{\mathrm{IV}}$	2.74
H(10)----N(4)	2.28	N(7)----N(7)$^{\mathrm{V}}$	3.14
O(4)	2.37	C(4)$^{\mathrm{V}}$	3.49
C(7)	2.90	C(15)$^{\mathrm{V}}$	3.48
C(17)----N(1)	3.37	N(8)----N(10)$^{\mathrm{VI}}$	3.25
N(3)	3.01	HN(10)$^{\mathrm{VI}}$	2.49
O(3)	3.24	H(22)----C(25)$^{\mathrm{VII}}$	2.82
H(17)----N(3)	2.40	C(26)$^{\mathrm{VII}}$	2.65
O(3)	2.56	H(19)----N(8)$^{\mathrm{VIII}}$	2.58
C(6)	2.97		
C(18)----N(1)	3.26		
O(1)	3.14		
O(3)	3.38		
C(19)----O(1)	3.44		
O(3)	3.25		
C(14)	3.43		
C(16)	3.46		
H(19)----O(3)	3.00		
H(17)	2.23		
C(23)----N(1)	3.24		
O(1)	3.25		
C(9)	3.08		
C(14)	3.30		
C(15)	3.13		
H(23)----C(9)	2.79		
C(15)	2.83		
H(9)	2.11		

*The Roman numerals as superscripts indicate equivalent positions relative to the reference molecule at x, y, z, as follows:

I	$-x,\ 1-y,\ 1-z$	V	$1-x,\ -y,\ -z$
II	$x,\ y,\ 1+z$	VI	$1+x,\ y,\ -1+z$
III	$-1+x,\ y,\ 1+z$	VII	$x,\ y,\ -1+z$
IV	$1-x,\ -y,\ 1-z$	VIII	$1-x,\ 1-y,\ -z$

[a] Limiting distances were taken as follows: O, N or C → O, N or C < 3.5 Å; O, N or C → H < 3.0 Å; H → H < 2.5 Å. These calculated distances do not include any involving the methyl hydrogens, but no exceptional contacts involving the methyl carbons were observed. The list does not include close atom–atom contacts which are an inevitable result of the basic molecular framework (such as *meta* and *para* distances in the phenyl). [b] These close contacts are imposed by the hydrogen bond between N(10) and O(3). [c] Contacts pertinent to the conformation of the cyclopentyl moiety have been omitted (see Discussion).

atom–atom repulsions are equalised. For example, distances such as C(12)–C(14), C(13)–C(14), C(15)–C(11) and C(16)–C(11) are all in the range 2.47–2.53 Å. The cyano groups, originating from the tetracyanoethylene, are in a staggered conformation, as are the hydrogens of the cyclopentyl moiety. Bond lengths and angles within this carbon ligand all appear normal (Table III).

The planar (Table IV) imidazole ligand (ref. 6 gives a review of some imidazole structure determinations) is perpendicular to the bisdimethylglyoximato moiety, and its projection on the [N_4] plane makes an angle of 19° with the line separating the two oximato units. The cobalt to glyoximato nitrogen atom bond-lengths, and the distances and internal bond-angles in the glyoximato moieties are generally unexceptionable [3, 5, 7]. However, a marked difference is found in the usually equivalent H-bonded distances: O(1)····H····O(3) = 2.52(1) Å, and O(2)····H····O(4) = 2.46(1) Å. The latter is near the lower limit of observed [3, 5, 7–11] O····H····O distances, and probably [8–10], but not certainly [7, 11], represents a symmetrical hydrogen bond. The weakening of the hydrogen bond between O(1) and O(3) seems a direct result of the further hydrogen bonding of O(3) to the N(10) of an adjacent molecule (Table III), with a probable contribution from a π-bond to the phenyl group.

Bound up with a discussion of these effects are a number of small distortions of the whole molecule. These are illustrated by Figure 2, which gives the projection of most of the non-hydrogen atoms of the molecule on the least-squares [N_4] plane (Table IV), and deviations (relative elevations) of many of the atoms from this plane.

Features include: (i) a 'tetrahedral' distortion of the bisdimethylglyoximato moiety (*cf.* relative elevations of the atoms in Figure 2); and (ii) the twist of the imidazole ligand, defined by the 19° angle which its projection on to the [N_4] plane makes with the line separating the two oximes.

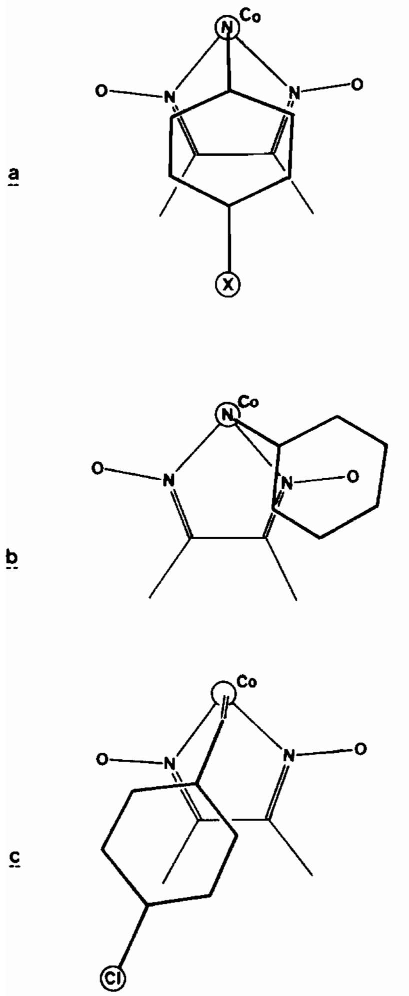

Figure 3. Projections of phenyl substituents of axial ligands on to the cobaloxime planes in other known structures. The axial ligands are: (a) sulphanilamide or 4-chloroaniline {X = SO_2NH_2, or Cl, ref. 7}; (b) aniline (ref. 13); and (c) C(Cl): $C(p\text{-}C_6H_4Cl)_2$ (ref. 5).

Pertinent to a discussion of these are the intra- and intermolecular atom–atom contacts listed in Table V.

For the imidazole, intermolecular contacts are less significant than the intramolecular ones. Thus it seems that the ligand is twisted away from its preferred line (zero 'twist') by the hydrogen bond to O(3′) until it is restrained by the close contacts of C(26)/H(26) and C(24)/H(24). The positions of N(2) and N(3) above the $[N_4]$ plane (Figure 2) seem also to be partially defined by these same forces (or these positions, defined by other forces, may simply allow a greater twist of the imidazole).

The tetrahedral distortion of the bisdimethylglyoximato moiety has two apparent sources: the H-bond O(3)····N(10) provides an attractive force to raise O(3) above the $[N_4]$ plane (Figure 2) whilst O(1) is held (below the plane) by the phenyl substituent of the carbanion ligand.

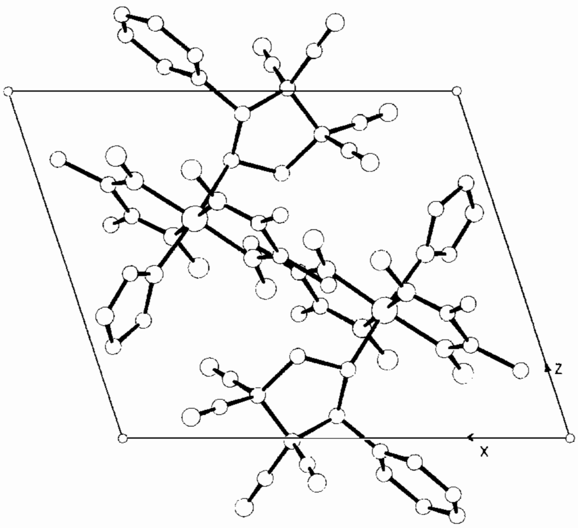

Figure 4. The packing of the molecules in the unit cell.

Structurally significant interactions involving the carbanion ligand appear to be:

(i) C(10)/H(10) are very close to N(4)/O(4) and C(17)/H(17) are close to N(3)/O(3).

(ii) H(9) lies between N(1) and N(2) and appears to be in a fairly narrow energy minimum.

(iii) The Co–C(9) bond is long, as noticed above.

(iv) The angles which C(9) makes at the cobalt show that the carbanion ligand is tipped a few degrees, apparently to minimise the interactions of (i).

(v) There are also a number of intermolecular close contacts (Table V) which may be important in defining the orientation of the ligand. However, it is impossible to take account of them without getting involved in a cyclic argument: the orientation may be defined by "crystal packing forces" without the result being evidenced by abnormally close atom–atom contacts. The only way of eliminating the effect of intermolecular forces seems to be the determination of the structures of a number of other related compounds.

(vi) Finally, there is the apparent π-bond of the phenyl substituent. It is very close to and almost parallel with the glyoximato plane; the perpendicular distance between planes is <3.0 Å {See Table IV, Plane (1)}; and the contacts between C(18)/C(23) and N(1)/O(1) are in the range 3.14–3.25 Å (Table V). These distances are significantly less than those observed in other molecular π-complexes [12].

Five other structures [5, 7, 13] of cobaloxime species show similar π-bonds between the glyoximato moieties and phenyl substituents on axial ligands: three are aniline [13] or substituted aniline [7] compounds, and there is one other carbanion compound [5], with two independent molecules. Figure

3 gives diagrams for each, showing the projections of the axial ligands on the cobaloxime planes, and hence the orientations of the phenyls with respect to the glyoximato moieties.

The aniline compounds have, of course, α phenyl substituents and the carbanion compounds so far studied have β phenyl substituents. This leads to angles between planes of ~25–30° in the aniline series [7, 13], and ~0–5° in the carbanions (present work and ref. 5).

For the latter, the three independent molecules show distortions of the cobaloxime moieties (*cf.* ref. 5) and these suggest a repulsion between glyoximate and phenyl. However, distances between planes are quite short at ~3.0 Å and, by contrast, in each case (Table IV and ref. 5) the carbon atom to which the phenyl is attached is displaced from the phenyl plane towards the cobalt: a distortion which indicates a bending of the phenyl *towards* the glyoximate.

The orientations of the phenyls in the known structures also show an interesting grouping. The aniline compounds have been discussed by Palenik *et al.* [7], especially from the viewpoint of the location of the glyoximato protons. One further point now emerges: in both series (Figure 3) the phenyls with electron-withdrawing substituents (Cl [5, 7] or SO_2NH_2 [7]) orient themselves above the hydrocarbon parts of the oxime ligands, whereas the unsubstituted phenyls (present work and ref. 13) are above oxime oxygens. This suggests a change from donor to acceptor role for the phenyls.

The packing of the molecules in the crystal is illustrated in Figure 4.

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