292. *X*-Ray Analysis of a Bridged Cobaloxime (Chloro-pyridino-*cis*-1,12-bis-methylglyoximato-dodecane-cobalt(III))

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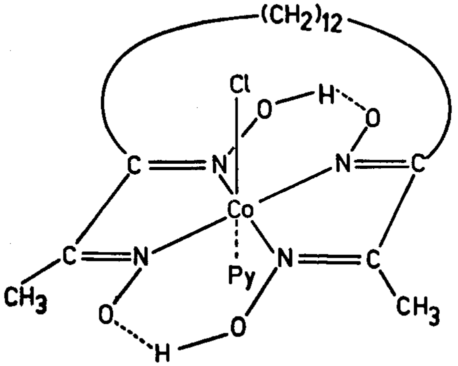
Summary. The structure of the title compound, a cobaloxime bridged by a polymethylene chain, has been confirmed by *X*-ray analysis.

In the preceding paper *Rétey* [1] has described the synthesis of bridged cobaloximes designed to provide a possible entry into the field of model compounds that might simulate the chemical behaviour of coenzyme-B_{12}-dependent enzymes. It seemed desirable to establish the structure of at least one of these bridged cobaloximes by *X*-ray analysis, especially since it was difficult to decide by other physico-chemical techniques whether the synthesis had led to the *cis*- or *trans*-arrangement of the two di-substituted glyoxime moieties. The compound chosen for *X*-ray analysis was the one with twelve methylene groups in the bridge; vaporometric measurements had suggested that this product might be dimeric, a possibility that could not be entirely excluded by the synthetic pathway. Our results show clearly that the compound has the constitution **1** with *cis*-arrangement of the substituents. The crystal packing does not indicate any marked tendency to dimerization or higher association of monomeric units. Details of the *X*-ray analysis are given below.



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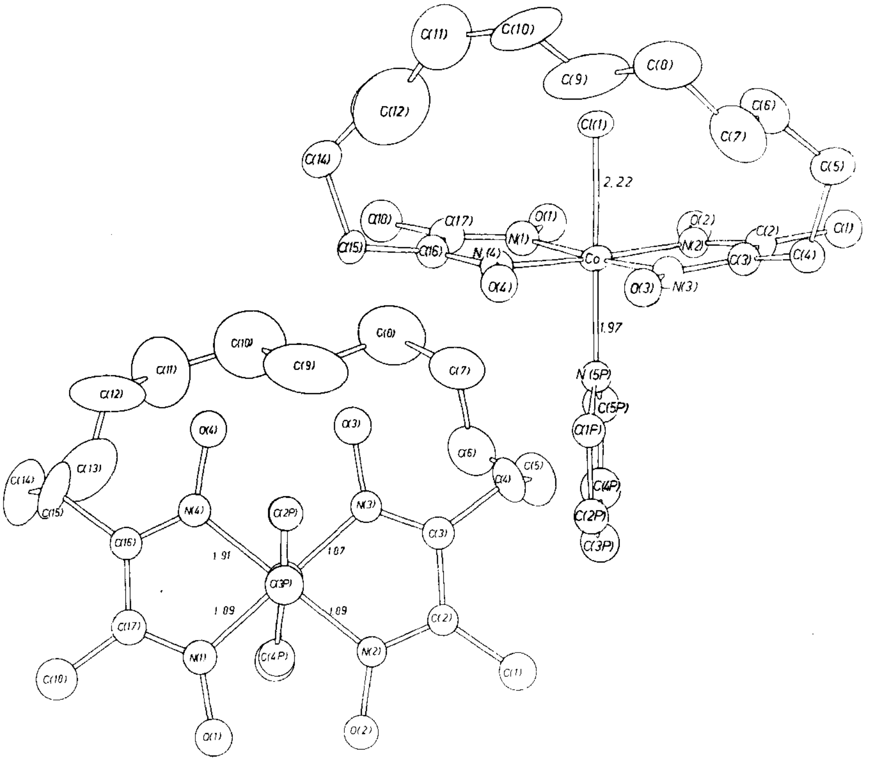
Crystal Data. Chloro-pyridino-*cis*-1,12-bis-methylglyoximato-dodecane-cobalt(III), $C_{23}H_{37}N_5O_4CoCl + CH_2Cl_2$, monoclinic, $a = 9.329$, $b = 27.127$, $c = 13.510$ Å, $\beta = 118.99°$, $U = 2990$ Å^3, $D_x = 1.37$, $Z = 4$, $D_m = 1.35$, space group $P\,2_1/c$, linear absorption coefficient $\mu(\mathrm{Mo}K_\alpha) = 8.1$ cm^{-1}. The sample provided by Dr. *J. Rétey* had been crystallized from methylene chloride/pentane solution. The crystals are brown prisms, elongated along [100].

Intensity Measurements. Intensities of 3285 independent reflexions were measured with a 4-circle diffractometer (*Hilger and Watts* Y 290, under control of a PDP-8 computer), using MoK_α radiation monochromatized by reflection from graphite. Intensities were converted to relative *F*-values in the usual way, absorption corrections being neglected.

Structure Analysis and Refinement. The structure was solved by a standard application of the heavy atom method, the only difficulty being the location of the polymethylene chain. Whereas the arrangement of the other (non-hydrogen) atoms was recognized without difficulty from the first Co-phased *Fourier* synthesis, the atoms in the chain had to be located step-by-step from successive syntheses based on increasingly complete phasing models. In a concluding (F_o–F_c)-synthesis from which the contributions of the central eight methylene groups to F_c were excluded, the peak densities of the corresponding carbon atoms (beginning and ending at a γ-methylene) were: 2.0, 1.6, 1.9, 1.9, 2.1, 2.3, and 2.1 $e/\text{Å}^3$. The density distributions associated with the central atoms are characterized not only by low peak density but also by pronounced anisotropy (see Figure). No other peaks higher than 0.5 $e/\text{Å}$ were present.



Two views of the molecule produced by computer programme ORTEP [3]
The ellipsoids were computed at 25% probability level

A series of full-matrix least-squares cycles led to a final R factor of 0.103, based on the 1971 reflexions with $F_o \geq 2.5\sigma(F_o)$ included with unit weights. In the final least-squares model, the vibration tensors of cobalt, chlorine and carbon atoms of the methylene chain were treated as anisotropic, those of the remaining carbon, nitrogen and oxygen atoms as isotropic. Hydrogen atoms were neglected.

Table 1. *Positional parameters x, y, z* (standard deviations in parentheses) *and isotropic thermal parameters* $U = 8\pi^2 B$ *from final least-squares refinement*

Atom	$x \cdot 10^4$	$y \cdot 10^4$	$z \cdot 10^4$	U (Å²) $\cdot 10^3$
Co	-1483 (3)	1143 (1)	1358 (2)	53*
Cl (1)	-4176 (5)	1124 (2)	695 (4)	70*
Cl (2)	-1805 (12)	3949 (4)	1241 (9)	172*
Cl (3)	-2393 (13)	4853 (4)	95 (9)	229*
O (1)	-1101 (15)	986 (5)	3562 (12)	82
O (2)	-1292 (14)	237 (5)	2446 (11)	69
O (3)	-1986 (15)	1300 (5)	-868 (12)	81
O (4)	-1796 (15)	2042 (5)	200 (12)	77
N (1)	-1268 (18)	1328 (6)	2776 (14)	67
N (2)	-1524 (16)	450 (5)	1473 (13)	52
N (3)	-1813 (16)	960 (5)	-74 (12)	57
N (4)	-1602 (17)	1844 (5)	1196 (14)	62
N (5P)	912 (15)	1147 (6)	1198 (12)	54
C (1P)	1539 (21)	1380 (7)	1376 (16)	63
C (2P)	3257 (23)	1380 (7)	1785 (17)	68
C (3P)	4215 (25)	1155 (9)	2778 (19)	87
C (4P)	3634 (26)	950 (8)	3494 (20)	93
C (5P)	1913 (23)	942 (8)	3027 (17)	77
C (1)	-1951 (24)	-377 (8)	565 (18)	81
C (2)	-1827 (20)	180 (7)	577 (16)	55
C (3)	-2051 (20)	494 (7)	-357 (16)	60
C (4)	-2575 (19)	301 (7)	-1524 (17)	79*
C (5)	-4437 (23)	163 (9)	-2162 (19)	112*
C (6)	-5605 (31)	580 (11)	-2312 (23)	132*
C (7)	-5622 (38)	932 (12)	-3075 (24)	155*
C (8)	-7087 (36)	1373 (17)	-3324 (32)	191*
C (9)	-6493 (42)	1712 (20)	-2239 (36)	227*
C (10)	-7509 (39)	2081 (16)	-2358 (39)	223*
C (11)	-6997 (48)	2455 (17)	-1334 (39)	227*
C (12)	-5383 (66)	2668 (18)	-350 (38)	250*
C (13)	-5045 (46)	2529 (14)	680 (42)	204*
C (14)	-3569 (30)	2783 (9)	1698 (29)	145*
C (15)	-1858 (21)	2643 (6)	1888 (20)	104*
C (16)	-1571 (21)	2089 (7)	2021 (17)	61
C (17)	-1368 (23)	1796 (8)	2926 (19)	71
C (18)	-1219 (28)	2001 (9)	3997 (21)	99
C (CH_2Cl_2)	-927 (29)	4418 (9)	807 (21)	102

* Equivalent mean isotropic U-values derived from the anisotropic U_{ij} tensors listed in Table 2.

Positional and thermal parameters of the atoms from the last least-squares cycle are given in Table 1. The atom-numbering scheme and bond distances involving cobalt are shown in the Figure.

Discussion. – Apart from those distances involving cobalt (shown in the Figure), the other interatomic distances and angles (not shown) are in general associated with such large estimated standard deviations that detailed discussion is not warranted. Within the rather large experimental uncertainties, the bond distances and angles of the glyoxime unit are in reasonable agreement with those found in a previously described substituted alkylcobaloxine structure [2]. The Co-N (pyridine) distance of 1.97 Å found in the present study is significantly shorter than the corresponding distance of 2.04 Å found there.

Table 2. *Components of* U_{ij} *in the expression* $\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)]$ *from final least-squares refinement*

	$U_{11}\cdot 10^3$	$U_{22}\cdot 10^3$	$U_{33}\cdot 10^3$	$U_{12}\cdot 10^3$	$U_{13}\cdot 10^3$	$U_{23}\cdot 10^3$
Co	49	57	74	-1	45	1
Cl (1)	48	75	96	0	42	-1
Cl (2)	226	126	230	-24	160	-2
Cl (3)	200	139	190	35	-32	-29
C (4)	59	107	63	-12	24	-37
C (5)	62	144	107	7	23	-27
C (6)	127	157	121	-49	68	-29
C (7)	182	167	113	-44	70	12
C (8)	100	264	167	18	30	27
C (9)	129	378	203	75	104	127
C (10)	131	289	294	76	139	48
C (11)	171	238	188	58	20	-17
C (12)	331	276	181	83	154	134
C (13)	172	144	335	79	154	62
C (14)	96	102	257	0	102	-41
C (15)	72	43	203	3	72	-27

The apparent bond lengths in the methylene chain range from 1.33 to 1.72 Å; the apparent torsion angles of the chain [starting at C(1)–C(2)–C(3)–C(4)] are: 5°, 74°, 59°, 69°, 175°, 72°, 177°, 30°, −113°, −172°, −71°, −56°, −70°, and −7°. The thermal vibration coefficients of the atoms involved are extremely large and in some cases highly anisotropic. These observations lead us to believe that the carbon atoms in the chain either vibrate with extremely large amplitude or that this part of the molecule is disordered – the chain conformation being somewhat different from molecule to molecule in the crystal. In either case the 'observed' atomic positions will not correspond to a reasonable instantaneous arrangement of the methylene groups. The two opposite extremities of the methylene chain are related by an approximate mirror plane, but the middle part deviates markedly from this symmetry, presumably to avoid a syn-planar partial conformation about the central bond.

The shortest intermolecular contact of 3.15 Å is between $C(CH_2Cl_2)$ and O(1). There are no contacts less than 3.75 Å between atoms in methylene chains of adjacent molecules. Thus there appears to be no tendency to form associated pairs of molecules in the crystal.

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