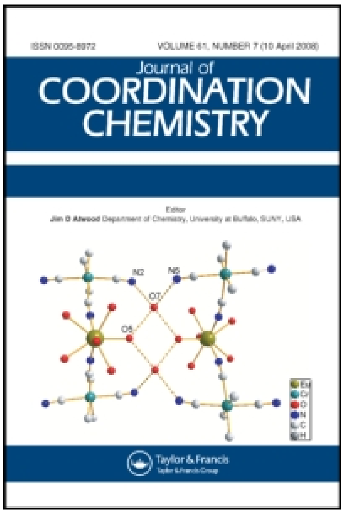

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

THE CRYSTAL AND MOLECULAR STRUCTURE TRANS-AZIDOBIS (DIMETHYLGLYOXIMATO) PYRIDINECOBALT(III)

Abraham Clearfield[a]; Ramanthan Gopal[a]; Robert J. Kline[a]; Mary L. Sipski[a]; Ludvik O. Urban[a]
[a] Department of Chemistry, Ohio University, Athens, Ohio, U.S.A.

To cite this Article Clearfield, Abraham , Gopal, Ramanthan , Kline, Robert J. , Sipski, Mary L. and Urban, Ludvik O.(1978) 'THE CRYSTAL AND MOLECULAR STRUCTURE TRANS-AZIDOBIS (DIMETHYLGLYOXIMATO) PYRIDINECOBALT(III)', Journal of Coordination Chemistry, 8: 1, 5 — 13

To link to this Article: DOI: 10.1080/00958977808073064

URL: http://dx.doi.org/10.1080/00958977808073064

J. Coord. Chem.
1978, Vol. 8, pp. 5–13

THE CRYSTAL AND MOLECULAR STRUCTURE TRANS-AZIDOBIS (DIMETHYLGLYOXIMATO) PYRIDINECOBALT(III)

ABRAHAM CLEARFIELD,[1] RAMANTHAN GOPAL, ROBERT J. KLINE, MARY L. SIPSKI and LUDVIK O. URBAN

Department of Chemistry, Ohio University, Athens, Ohio 45701, U.S.A.

(Received September 1, 1977)

Crystals of trans-azidobis(dimethylglyoximato)pyridinecobalt(III) are monoclinic, space group $P2_1/c$. The unit cell constants are a = 8.731(3), b = 13.982(3), c = 17.961(5) Å, β = 126.80(1), V = 1755.7 Å^3, and Z = 4. The structure was determined from three dimensional X-ray data (2152 independent reflections) obtained by the $\theta - 2\theta$ scan method using a CAD–4 automated four-circle diffractometer. Structure solution was effected by Patterson and Fourier methods and refined by block diagonal least squares method to a conventional R value of 0.041. The two dimethyl glyoximato monoanions occupy the equatorial plane with pyridine and azide groups in the axial positions. Azide N–N bond distances were found to be 1.155(6) and 1.126(7) Å with the longer bond adjacent to the cobalt atom. Cobalt–nitrogen bonds in the axial positions are significantly longer than those in the equatorial plane. Although the O–O interatomic distances between the separate oxime anions are close to 2.5 Å the hydrogen bonding is decidedly unsymmetrical.

INTRODUCTION

Among the best studied cobaloximes are complexes of the type $LCo(DH)_2X$ where DH is the monoanion of dimethylglyoxime, L is a donor molecule and X is an anion ligand. Compounds of this type have been shown to mimic the chemistry of the cobalt atom in corrins and therefore have been used extensively as models of Vitamin B_{12} compounds.[2-4] The relevant aspects of these chemical analogies with Vitamin B_{12} compounds reside in the reactivity of the axial positions and in the electronic effects transmitted through the metal atom (i.e. ground state, thermodynamic and kinetic *cis* and *trans* effects).

Conventional methods of analysis such as infrared, ultraviolet and visible spectrophotometry have often been used to elucidate cobaloxime systems.[5-6] The occurrence of planar hydrogen bonding in the $Co(DH)_2^+$ moiety and hence the trans octahedral geometry of $Co(DH)_2LX$, can be conveniently demonstrated from infrared data.[7-9] The characteristic O . . . H . . . O bending frequency occurs in the region 1700–1800 cm^{-1} and the stretching vibration at ~2300 cm^{-1}. Thus infrared spectroscopy has been frequently used to establish the trans octahedral geometry. Recently the geometry of several cobaloximes has been established unequivocally by means of single crystal X-ray studies.[10-11]

It occurred to us that a study of the structure of azido cobaloximes of the type $[Co(DH)_2PyN_3]$ could shed some light on the cis and trans bonding interactions. The N_3^- ligand coordinates in angular manner through a terminal N atom and the two azide N–N bond distances provide an indication of the interaction with the metal center. A comparison of the bonding parameters of the two complexes $[Co(DH)_2PyN_3]$ and $[Co(BAE)PyN_3]$ was reported upon earlier.[12] Structural details of the former compound are presented in this paper together with infrared data for both complexes.

EXPERIMENTAL SECTION

Preparation of trans-Azidobis(dimethylglyoximato)-pyridinecobalt(III)

$(PyCo(DH)_2N_3)$. To a hot solution of 5.5 g (47.0 mmol) of dimethylglyoxime in 200 ml of methanol was added 5.24 g (21.0 mmol) of cobalt(II) acetate tetrahydrate with stirring to form a dark maroon solution. Then 3.44 g (43.0 mmol) of pyridine was added (the solution turned brown) followed immediately by 1.36 g (21.0 mmol) of sodium azide dissolved in 20 ml of water. After cooling the reaction mixture to room temperature a stream of air was blown through for 30 minutes during which time the product crystallized. The brown crystals were collected by filtration, washed successively with 50 ml portions of water, 95% ethanol, and diethyl ether, and dried at room temperature *in vacuo.* The yield was 6.1 g (71% based on cobalt(II) acetate tetrahydrate). The product was recrystallized from 95% ethanol. Analysis: Calculated for $C_{13}H_{19}N_8O_4Co$: (M.W. 410.28) C, 38.06%; H, 4.67%; N, 27.31%. Found: C, 38.39%; H, 4.50%; N, 27.28%.

Crystal and X-ray Data Collection

The original crystals were recrystallized from 95% ethanol to yield shiny, henna colored air-stable platelets suitable for X-ray studies. Preliminary survey photographs taken by both the Weissenberg and precession methods revealed a monoclinic unit cell with the following systematic absences: (OkO) for k = 2n + 1 and (hOl) for $\ell = 2n + 1$. These absences are consistent with the space group $P2_1/c$. Accurate unit cell dimensions were obtained with the aid of a CAD–4 automated 4-circle diffractometer (Enraf-Nonius). The crystal chosen for data collection measured 0.12 x 0.15 x 0.20 mm and was mounted with the needle axis approximately parallel to the Φ axis of the goniometer. Forty-one reflections at high and moderate Bragg angles were scanned using a graphite monochromator and 4° take-off angle with Mo Kα (λ = 0.70926 Å) radiation. The Bragg angles were accurately determined by use of the program DETCELL[13] and unit cell dimensions obtained by least-squares calculations using a locally written program.[14] The results were a = 8.731(3), b = 13.982(3), c = 17.961(5) Å, β = 126.80(1)°, V = 1755.7 Å^3. The density, determined by flotation in an aqueous solution of sodium chloride, was found to be 1.54 g/cm^3. This compares to a calculated density, with Z = 4 and F.W. 410.3, of 1.553 g/cm^3.

Intensities were collected in the $\pm h +k +\ell$ octants out to a maximum Bragg angle of 32°. Data were measured by the $\theta-2\theta$ scan technique using a variable 2θ scan rate given by

$$\text{Scan Rate} = 20.1166 / X \text{ deg min}^{-1}$$

where X is an integer determined by the intensity of the reflection being scanned. X had a minimum value of 2 for intense reflections and a maximum value of 38 for very weak ones. A continuously variable aperture ranging in horizontal width from 2.11 to 3.00 mm was used. The aperture width was controlled by the computer as was the insertion of attenuators when a counting rate in excess of 50,000 counts/second was sensed. The scan width (angular range) was also variable and equal to 3 times (0.6 + 0.2 tan θ) deg. The right and left backgrounds were each scanned at ¼ the total scan time. A total 6090 independent reciprocal lattice points were thus scanned, including three standard reflections of high, medium and low intensity which were scanned every 24 reflections. The fluctuation of the standards was random and amounted to ±4% overall. The set of data was corrected for these fluctuations by assuming a linear change in the intensity of the standards between two consecutive measurements.[15] Only those reflections whose net counts determined as NET = TOTAL CTS. – 2(R + L) BKGD. CTS. were greater than or equal to 3σ where σ = (TOTAL CTS. + BKGD. CTS.)$^{1/2}$ were considered observed. A total of 2152 observed reflections were thus obtained. These were corrected for Lorentz and double polarization effects.[16] No correction for absorption was made since μR (μ = 10.56 cm^{-1}) ranged from 0.063 to 0.106 (A = .94–.90).

Structure Solution and Refinement

A three dimensional Patterson map revealed the positions of the cobalt atom and the atoms bonded to it together with six carbon atoms. The remaining non-hydrogen atoms were obtained from successive Fourier and difference maps. Least-squares refinement of the positional parameters with isotropic temperature factors by the block-diagonal method[17] gave R = 0.073 where $R = \Sigma \,||Fo| - |Fc||/\Sigma |Fo|$. Anisotropic refinement, however, lowered the residual index to 0.051.

Most of the hydrogens were found on electron-density difference maps at this point with peak heights having minimum and maximum values of about 0.27 and 0.48 eÅ^{-3}, respectively. However, the hydrogen atom positions, except for those of methyl hydrogens, were idealized at distances of 0.95 Å from the carbon atoms and making the proper angles (109.5° for tetrahedral carbons, etc.) with them. In the case of the methyl groups the two best hydrogen atom positions were retained and the third calculated for ideal tetrahedral geometry. The hydrogen atoms were included in subsequent structure factor calculations with their coordinates fixed and isotropic thermal parameters set one unit higher than that of

TABLE I
Final positional parameters with isotropic temperature factors

Atom	x	y	z	$\beta_{(iso)}$
Co(1)	0.28043(10)	−0.15616(6)	0.28754(5)	2.22
N(1)	0.2694(6)	−0.0295(3)	0.3218(3)	3.06
N(2)	0.2512(6)	−0.0901(3)	0.1868(3)	2.95
N(3)	0.2857(6)	−0.2832(3)	0.2524(3)	3.87
N(4)	0.3007(6)	−0.2218(3)	0.3865(3)	3.68
N(5)	0.0036(6)	−0.1658(4)	0.2203(3)	4.06
N(6)	−0.1020(6)	−0.1529(4)	0.1411(3)	4.25
N(7)	−0.2161(7)	−0.1408(6)	0.0647(3)	7.65
N(8)	0.5611(5)	−0.1466(3)	0.3610(3)	2.57
O(1)	0.2765(6)	−0.0104(3)	0.3964(3)	4.59
O(2)	0.2380(5)	−0.1371(3)	0.1180(3)	3.69
O(3)	0.2795(6)	−0.3032(3)	0.1775(3)	4.91
O(4)	0.3065(5)	−0.1761(3)	0.4535(3)	3.78
C(1)	0.3059(9)	−0.3745(5)	0.4533(4)	4.78
C(2)	0.3005(8)	−0.3128(4)	0.3839(4)	3.52
C(3)	0.2908(8)	−0.3495(5)	0.3043(4)	3.87
C(4)	0.2827(11)	−0.4549(4)	0.2831(5)	5.59
C(5)	0.2160(9)	0.0641(5)	0.1138(5)	5.00
C(6)	0.2437(8)	0.0019(4)	0.1885(4)	3.73
C(7)	0.2551(8)	0.0376(4)	0.2685(4)	3.26
C(8)	0.2546(11)	0.1408(5)	0.2881(5)	5.21
C(9)	0.6506(6)	−0.1609(5)	0.3220(3)	3.62
C(10)	0.8482(7)	−0.1542(5)	0.3732(4)	3.44
C(11)	0.9565(7)	−0.1336(5)	0.4654(4)	3.43
C(12)	0.8655(8)	−0.1186(5)	0.5055(4)	4.42
C(13)	0.6694(8)	−0.1255(5)	0.4518(4)	4.15

the corresponding carbon atoms to which they are bonded. When convergence was achieved, a final difference map revealed the positions of the hydrogen bridge atoms in the DH groups. These were then refined in the last two least squares cycles. The final set of agreement parameters were thus obtained: R = 0.041, Rw = 0.031, where the weighted R-index (Rw)[18] is defined as

$$Rw = [\Sigma w(|Fc| - |Fo|)^2/\Sigma w|Fo|^2]^{1/2}$$

The weighting scheme used in the refinement assigned weights as

$$w = \frac{1}{[1 + [(|Fo| - P_2)|P_1]^2]}.$$

P_1 and P_2 were set at 50 and 175, respectively. The function minimized was $\Sigma w(|Fo| - |Fc|)^2$. Neutral atom scattering factors, as listed by Hanson, *et al.*[19] and corrected for anomalous dispersion were used in the refinement. Hydrogen atom scattering factors were those given by Stewart *et al.*[20]

In the last cycle all the shifts for the non-hydrogen atoms were less than one-tenth of their corresponding standard deviations. A difference Fourier was featureless with no maxima above + 0.3 e/Å^3. The final positional and isotropic thermal parameters for the non-hydrogen atoms are given in Table I while the anistropic thermal parameters are listed in Table II. Hydrogen atom data are given in Table III. A listing of observed and calculated structure factors is available upon request.

RESULTS AND DISCUSSION

Figure 1 shows a schematic drawing of the molecule with the numbering system used while Figure 2 represents the thermal motion of atoms within the complex. Two dimethylglyoxime monoanions occupy the equatorial plane and are coordinated to cobalt through nitrogen atoms. The octahedral coordination is completed by pyridine and azide groups in the axial sites. Bond distances and angles are given in Tables IV and V, respectively.

The two dimethylgloximate ligands are identical within two standard deviations. Chakravorty has provided a comprehensive summary of the structural parameters for transition metal oximes.[21] Bond distances obtained in this study for the coordinated dimethylglyoxime ligands fall within the range found for similar structures. It should be noted that the

TABLE II
Anisotropic thermal parameters for nonhydrogen atoms ($X10^4$)[a]

	β_{11}	β_{22}	β_{33}	$2\beta_{12}$	$2\beta_{13}$	$2\beta_{23}$
Co(1)	111(1)	36.9(3)	28.8(3)	−8(2)	74(1)	−2.5(9)
N(1)	144(9)	43(3)	42(3)	23(9)	108(9)	−1(5)
N(3)	152(10)	42(3)	39(3)	−29(9)	86(9)	−20(5)
N(4)	138(9)	51(3)	36(3)	−1(9)	97(9)	11(5)
N(2)	137(10)	53(3)	28(2)	−9(9)	79(8)	1(5)
N(5)	115(9)	72(4)	43(3)	−20(11)	74(9)	14(6)
N(6)	122(9)	59(3)	50(3)	12(11)	84(9)	13(6)
N(7)	185(12)	198(8)	56(4)	20(22)	76(12)	48(10)
N(8)	108(8)	34(3)	34(2)	−2(9)	80(7)	−8(4)
O(1)	247(10)	56(3)	48(3)	28(9)	162(9)	−12(4)
O(4)	219(9)	63(3)	44(2)	25(9)	151(8)	10(4)
O(3)	269(11)	55(3)	46(2)	−42(10)	148(9)	−33(4)
O(2)	246(10)	64(3)	35(2)	−12(9)	128(8)	−10(4)
C(2)	146(12)	55(4)	45(3)	−2(12)	104(11)	19(6)
C(3)	148(11)	43(3)	58(4)	−16(14)	107(12)	4(7)
C(6)	134(12)	48(4)	40(3)	186(12)	90(11)	19(6)
C(7)	139(12)	39(3)	50(4)	15(11)	105(12)	10(6)
C(1)	258(18)	82(6)	71(5)	17(17)	181(17)	59(9)
C(4)	306(18)	39(4)	84(5)	−34(17)	188(17)	−4(9)
C(5)	270(18)	65(5)	59(4)	23(16)	162(16)	46(8)
C(8)	407(21)	45(5)	86(5)	35(18)	272(18)	18(9)
C(9)	148(11)	41(3)	38(3)	1(12)	105(9)	−8(6)
C(10)	170(12)	48(4)	49(3)	21(14)	137(11)	6(7)
C(11)	105(11)	64(5)	46(3)	−9(11)	81(11)	−7(7)
C(12)	162(13)	89(6)	35(3)	4(15)	77(12)	−21(7)
C(13)	147(12)	71(5)	37(13)	−10(13)	98(11)	−20(6)

[a] The form of the thermal ellipsoid equation is

$$\exp\left[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)\right]$$

average C–N bond distance in the oxime 1.288(3) Å, is somewhat smaller than that in the pyridine moiety (1.340(1) Å) indicating a bond order >1½. Cobalt–nitrogen bonds formed by the axial ligands are significantly longer than those in the equatorial position. This is to be expected based upon prior studies.[11-12]

The ligand–cobalt–ligand bond angles in the equatorial plane consist of two which are larger than 90° (N(1)–Co–N(4) type and two which are smaller (N(1)–Co–N(2) type). This undoubtedly results from the steric requirements of the five membered rings and hydrogen bonding in the six membered rings. A similar distribution of angles in the equatorial plane has been observed in other dimethylglyoximates.[10, 11, 22] In trans-azidobis(acetylacetonatoethylenediimine)pyridinecobalt(III), where all the rings in the equatorial plane are five-membered, the opposite distribution of angles is observed.[12] All the other angles in the coordination octahedron are very close to 90°.

Hydrogen bond parameters are given in Table VI. Chakravorty has indicated that oximes in which the

TABLE III
Positional parameters for hydrogen atoms

Atom	x	y	z	B_{iso}
H(1)	0.275	−0.095	0.429	5.5
H(2)	0.275	−0.214	0.147	5.5
H(3)	0.275	−0.428	0.426	5.8
H(4)	0.214	−0.354	0.464	5.8
H(5)	0.429	−0.375	0.513	5.8
H(6)	0.403	−0.486	0.331	6.6
H(7)	0.269	−0.465	0.225	6.6
H(8)	0.184	−0.489	0.280	6.6
H(9)	0.114	0.119	0.074	6.0
H(10)	0.195	0.023	0.067	6.0
H(11)	0.333	0.099	0.141	6.0
H(12)	0.267	0.191	0.260	6.2
H(13)	0.360	0.150	0.353	6.2
H(14)	0.134	0.154	0.280	6.2
H(15)	−0.422	−0.177	0.256	4.6
H(16)	−0.086	−0.163	0.344	4.4
H(17)	0.094	−0.129	0.500	4.4
H(18)	−0.053	−0.105	0.571	5.4
H(19)	−0.392	−0.113	0.483	5.1

TABLE IV
Interatomic distances (Å)

Co–N(1)	1.896(5)	Co–N(3)	1.896(5)
Co–N(2)	1.908(5)	Co–N(4)	1.913(5)
Co–N(5)	1.955(6)	Co–N(8)	1.973(5)
N(5)–N(6)	1.155(6)	N(6)–N(7)	1.126(7)
N(1)–O(1)	1.331(7)	N(4)–O(4)	1.336(6)
N(2)–O(2)	1.342(6)	N(3)–O(3)	1.342(7)
O(1)–H(1)	1.325(40)	O(3)–H(2)	1.350(40)
O(4)–H(1)	1.189(40)	O(2)–H(2)	1.154(40)
N(1)–C(7)	1.292(8)	N(4)–C(2)	1.273(8)
C(7)–C(6)	1.466(9)	C(2)–C(3)	1.472(9)
C(6)–N(2)	1.289(8)	C(3)–N(3)	1.296(8)
C(5)–C(6)	1.493(9)	C(1)–C(2)	1.494(10)
C(7)–C(8)	1.485(8)	C(3)–C(4)	1.514(9)
N(8)–C(9)	1.341(8)	N(8)–C(13)	1.339(7)
C(9)–C(10)	1.389(9)	C(12)–C(13)	1.376(10)
C(10)–C(11)	1.358(8)	C(11)–C(12)	1.370(10)

TABLE V
Bond angles (deg)

N(1)–Co–N(2)	81.5(2)	N(3)–Co–N(4)	81.5(2)
N(1)–Co–N(3)	178.7(6)	N(2)–Co–N(4)	178.1(2)
N(1)–Co–N(4)	98.1(2)	N(2)–Co–N(3)	98.8(2)
N(1)–Co–N(5)	88.9(2)	N(1)–Co–N(8)	90.2(2)
N(2)–Co–N(5)	92.0(2)	N(2)–Co–N(8)	90.5(2)
N(3)–Co–N(5)	89.8(2)	N(3)–Co–N(8)	91.1(2)
N(4)–Co–N(5)	86.2(2)	N(4)–Co–N(8)	91.4(2)
N(5)–Co–N(8)	177.3(2)		
N(5)–N(6)–N(7)	174.6(7)	Co–N(5)–N(6)	122.0(5)
Co–N(1)–C(7)	116.1(4)	Co–N(4)–C(2)	116.6(4)
Co–N(1)–O(1)	122.2(4)	Co–N(4)–O(4)	122.7(4)
Co–N(2)–C(6)	116.1(4)	Co–N(3)–C(3)	115.3(4)
Co–N(2)–O(2)	121.7(4)	Co–N(3)–O(3)	122.3(6)
O(1)–N(1)–C(7)	121.7(5)	O(4)–N(4)–C(2)	120.7(5)
N(1)–C(7)–C(8)	122.8(6)	N(4)–C(2)–C(1)	122.6(5)
N(1)–C(7)–C(6)	113.4(5)	N(4)–C(2)–C(3)	112.4(5)
C(8)–C(7)–C(6)	123.7(6)	C(1)–C(3)–C(3)	123.4(6)
C(7)–C(6)–C(5)	124.2(6)	C(4)–C(3)–C(2)	123.9(6)
C(7)–C(6)–N(2)	112.9(6)	C(2)–C(3)–N(3)	114.1(6)
C(6)–N(2)–O(2)	122.2(5)	C(3)–N(3)–O(3)	122.5(5)
C(5)–C(6)–N(2)	122.7(6)	C(4)–C(2)–N(3)	122.6(6)
C(10)–C(9)–N(8)	121.6(5)	N(8)–C(13)–C(12)	133.9(6)
C(9)–C(10)–C(11)	120.2(6)	C(13)–C(12)–C(11)	119.4(6)
C(10)–C(11)–C(12)	118.3(6)	C(9)–N(8)–C(13)	117.6(5)

TABLE VI
Hydrogen bonding distances (Å) and angles (deg)

O(4)–H(1)	1.19(4)	O(2)–H(2)	1.15(4)
O(1)–H(1)	1.32(4)	O(3)–H(2)	1.35(4)
O(1)–O(4)	2.483(6)	O(2)–O(3)	2.500(6)
N(1)–O(1)–H(1)	105.5(4)	N(2)–O(2)–H(2)	100.7(4)
O(1)–H(1)–O(4)	163(2)	O(2)–H(2)–O(3)	168(2)
H(1)–O(4)–N(4)	104.9(4)	H(2)–O(3)–N(3)	100.5(4)

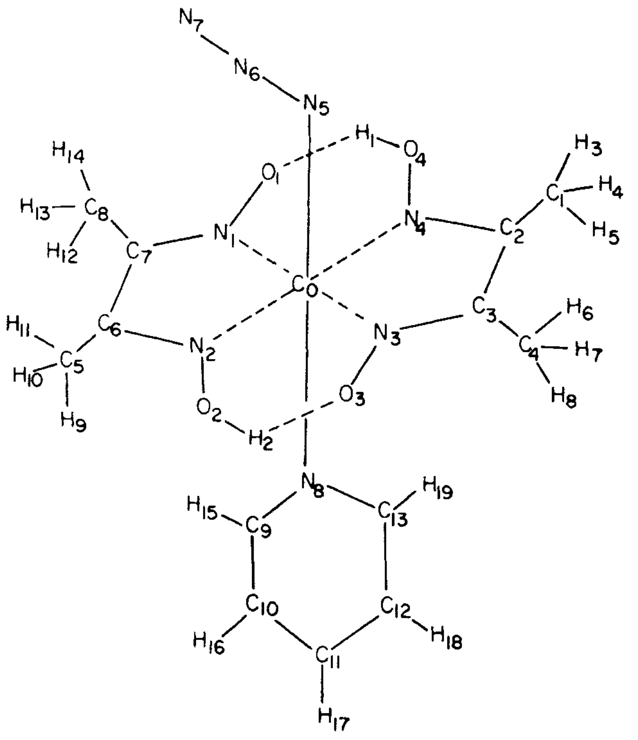

FIGURE 1 Schematic of [Co(DH)$_2$PyN$_3$] showing the numbering system used in the tables.

O . . . O distance is less than 2.5 Å have a symmetrical hydrogen bond.[21] In the present structure the O . . . O distances are very close to this value but the hydrogen bonds are definitely unsymmetrical. Furthermore, the N–O distances are equal in disagreement with the idea that the N–O distance is a sensitive indicator of the bridging proton position in complexes of this type.[10, 22]

Mean plane equations are presented in Table VII. Each plane formed by two nitrogens and two carbons of the glyoximate groups (Planes 1 and 2), which together with cobalt form the five-membered chelate rings, are perfectly planar. However, the Co atom lies 0.049 Å below Plane 1 and 0.069 Å above Plane

TABLE VII
Mean planes and distances of selected atoms therefrom (Å)

A. Plane 1 formed by N(1), N(2), C(6), C(7)

$+0.8403x + 0.0426y + 0.5404z = 1.5516 \quad x^2 = 0.145$

N(1)	+0.001(6)	C(6)	+0.002(7)
N(2)	−0.001(6)	C(7)	−0.002(7)

Other atoms

Co	−0.048(1)	O(2)	0.037(5)
O(1)	0.033(5)	N(5)	1.902

B. Plane 2 formed by N(3), C(3), C(2), N(4)

$-0.8271x + 0.0022y - 0.5620z = -1.8648 \quad x^2 = 0.283$

N(3)	−0.001(6)	C(2)	−0.002(7)
N(4)	+0.001(6)	C(3)	+0.002(7)

Other atoms

Co	0.069(1)	O(4)	0.016(5)
O(3)	−0.018(5)		

C. Plane 3 formed by N(1), N(2), N(3), N(4), C(2), C(3), C(6), C(7)

$-0.8383x - 0.0452y - 0.5433z = -1.5664 \quad x^2 = 110$

N(1)	0.001(6)	N(3)	−0.042(6)
N(2)	0.010(6)	N(4)	−0.029(6)
C(6)	0.008(7)	C(2)	0.027(7)
C(7)	−0.001(8)	C(3)	0.026(8)

Other atoms

Co	−0.041(1)		
O(1)	0.027(5)	O(2)	0.053(5)
O(4)	−0.019(5)	O(3)	−0.074(5)
H(1)	0.133(8)	H(2)	−0.131(8)

D. Plane 4 formed by Co, N(1), N(2), N(3), N(5)

$-0.8399x - 0.0586y - 0.5395z = -1.5406 \quad x^2 = 450$

Co	−0.021(1)		
N(1)	0.000(6)	N(3)	0.000(6)
N(2)	0.010(6)	N(4)	0.010(6)

E. Pyridine plane

$0.0621x + 0.9745y - 0.2154z = -3.0509 \quad x^2 = 0.92$

N(8)	−0.002(4)	C(11)	−0.004(6)
C(9)	−0.001(6)	C(13)	0.002(7)
C(10)	0.004(6)	C(12)	0.000(7)

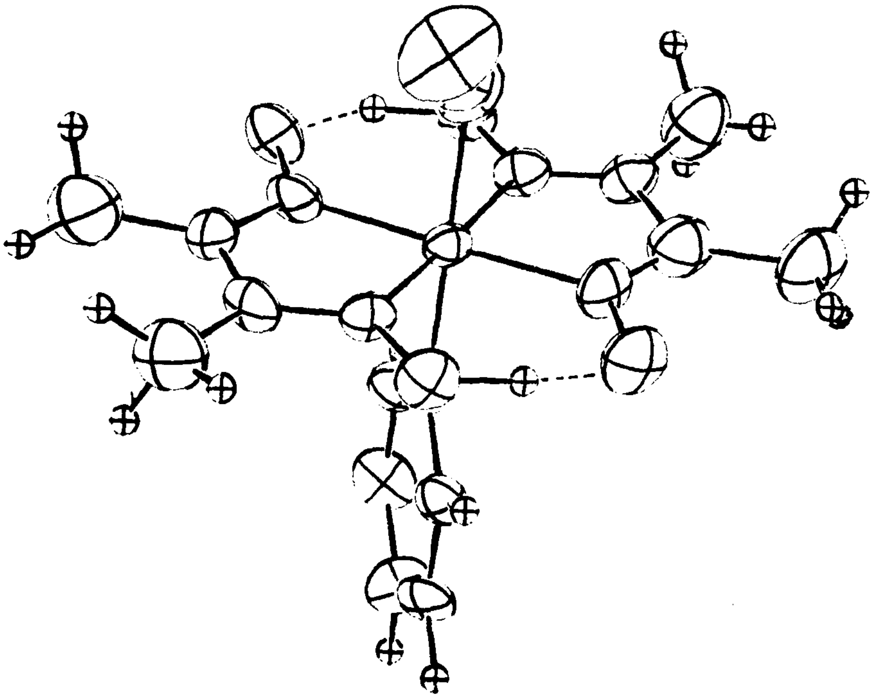

FIGURE 2 A perspective view showing the thermal ellipsoids at the 50% probability level.

2. This comes about because the two planes are inclined towards each other making a dihedral angle of 2.9°. Examination of the deviations from the equatorial plane formed by all eight atoms (Plane 3) shows that Plane 1 roughly coincides with the equatorial Plane 3 while Plane 2 is tilted away from the horizontal towards the azide group. The tilt is such that the nitrogen atoms are below the equatorial plane and the carbon atoms above it. Another interesting feature is the positioning of the hydrogen bonded atoms. O(1) and O(2) are above the plane while O(3) and O(4) are below it. However one hydrogen atom (H(1)) lies 0.13 Å above the plane while the other is 0.13 Å below it. All the nitrogen atoms in the equatorial plane lie above the cobalt (on the side of the azide group) as can be seen by the deviations from Plane 4.

Azide groups bonded covalently to metals are unsymmetrical. A table of representative bond distances was presented in our earlier paper.[12] Since the difference in N–N bond lengths in the present case exceeds 3σ, and the longer bond is adjacent to the cobalt atom, it can safely be assumed that this azide is unsymmetrical and the metal–azide bond is possessed of covalent character. The Co–N–N angle is 122.0(5)° and the N–N–N angle is 174.6(7)°. The dihedral angle between the planes formed by Co–N_3 and the pyridine ring is 26.2°. This is much smaller than the value (67.8°) in the corresponding bis(acetylacetonatoethylenediimine) complex.[12]

No intermolecular contacts of less than 3 Å were found. Thus, the crystal consists of independent molecular units. A packing diagram is shown in Figure 3.

A linear correlation between Δd, the difference between the two N–N distances in some coordinated metal azides and the azide infrared stretching frequencies has been discovered.[23] The larger is Δd, the higher is the frequency of the antisymmetric stretch and the lower is the frequency of the symmetric stretching vibration. The azide bending mode has not been so correlated as it is less diagnostic of the azide bonding. A comparison of infrared structural information for the two complexes [$Co(DH)_2PyN_3$] and [$Co(BAE)PyN_3$] can now be made. The relevant data are presented in Table VIII where one may note that the azide infrared bonds for the two complexes are virtually identical in spite of an almost 2 to 1 ratio in the Δd values. The errors in Δd, however, remove some of the force of this argument as the real difference in the two Δd values may be considerably smaller. In any case our bond

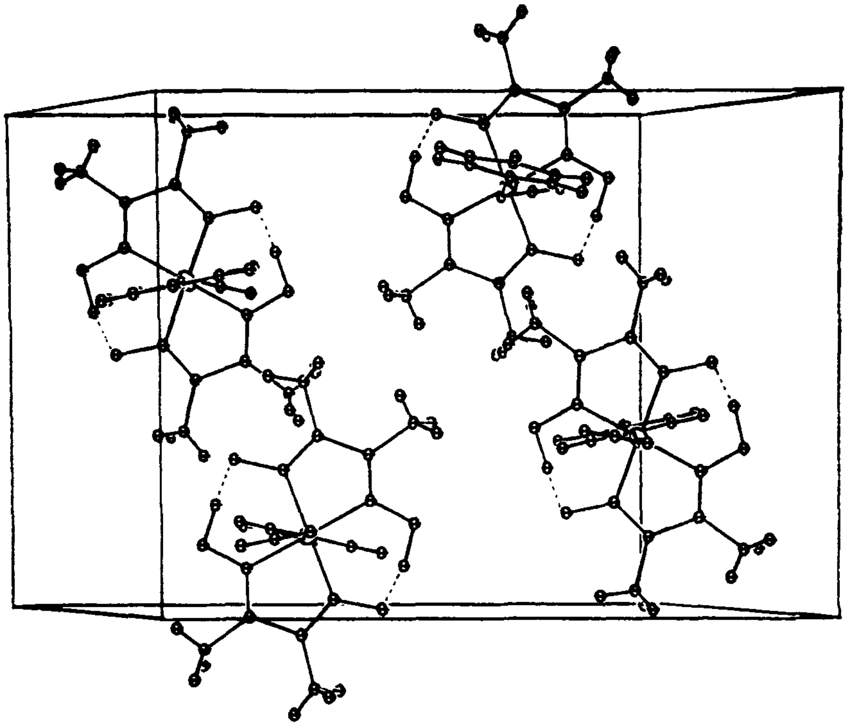

FIGURE 3 Packing diagram of unit cell contents.

TABLE VIII
Azide bond distances and infrared frequencies

Bond distance (Å) or vibration (cm^{-1})[a]	[Co(BAE)PyN$_3$]	Δd	[Co(DH)$_2$PyN$_3$]	Δd
$M\overset{\downarrow}{-}N-N$	1.186(8)		1.155(6)	
$M-N\overset{\downarrow}{-}N$	1.133(9)	0.053	1.126(7)	0.029
νas	2022 vs		2018 vs	
νs	1278 s		1279 s	
δN_3	639 m		642 w	

[a] Mineral oil mull spectral data.

distances were determined to a greater accuracy than those used to construct the correlation[23] but do not fit the linear relationship given by Agrell.[23]

REFERENCES

1. Present address, Department of Chemistry, Texas A&M University, College Station, Texas 77843.
2. G. N. Schrauzer and J. Kohnle, *Chem. Ber.*, 97, 3056 (1964).
3. G. N. Schrauzer and R. J. Windgassen, *Chem. Ber.*, **99**, 602 (1966).
4. G. N. Schrauzer, *Accounts Chem. Res.*, 1, 97 (1968).
5. H. A. Hill and K. G. Morallee, *J. Chem. Soc., A*, 554 (1969).
6. G. De Alti, V. Galasso and A. Bigotto, *Inorg. Chem. Acta.*, 3, 527 (1969).
7. G. N. Schrauzer and R. J. Windgassen, *J. Amer. Chem. Soc.*, **88**, 3738 (1966).
8. R. D. Gillard and G. Wilkinson, *J. Chem. Soc., London*, 6041 (1963).
9. Z. Finta, Cs. Varhelyi and J. Zsako, *J. Inorg. Nucl. Chem.*, **32**, 3013 (1970).
10. D. L. McFadden and A. T. McPhail, *J. Chem. Soc., Dalton*, 363 (1974).
11. S. Bruckner and L. Randaccio, *J. Chem. Soc., Dalton*, 1017 (1974).

12. A. Clearfield, R. Gopal, R. J. Kline, M. L. Sipski and L. O. Urban, *J. Coord. Chem.*, (in press).
13. Enraf-Nonius. Instruction manual for CAD-4 system, Delft, Holland (1972).
14. G. D. Smith, Cell dimensions-least squares program, Ohio University Crystallography Laboratory, Athens, Ohio (1968).
15. R. W. Olson, CAD-4 output tape process, Ohio University Crystallography Laboratory, Athens, Ohio (1973).
16. U. W. Arndt and B. T. M. Willis, Single crystal Diffractometry, p. 286, Cambridge: Cambridge Univ. Press (1966).
17. The programs used in this study other than those listed individually were those of F. R. Ahmed, S. R. Hall, M. E. Pippy and C. P. Huber, NRCC crystallographic programs for the IBM/360, National Research Council of Canada, Ottawa, Canada.
18. W. C. Hamilton, *Acta Cryst.*, **18**, 502 (1965).
19. H. P. Hanson, F. Herman, J. D. Lea and S. Skillman, *Acta Cryst.*, **17**, 1040 (1964).
20. R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
21. A. Chakravorty, *Coord. Chem. Rev.*, **13**, 46 (1974).
22. K. Bowman, A. P. Gaughan and Z. Dori, *J. Amer. Chem. Soc.*, **94**, 727 (1972).
23. R. I. Agrell, *Acta. Chem. Scand.*, **25**, 2965 (1971).