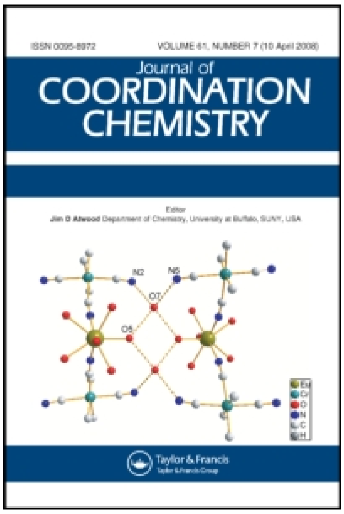

**Journal of Coordination Chemistry**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

# THE CRYSTAL STRUCTURE OF trans-AZIDOBIS (ACETYLACETONATO)ETHYLENEDIIMINEPYRI-DINECOBALT(III)

Abraham Clearfield[a]; Ramanathan Gopal[a]; Robert J. Kline[a]; Marilee Sipski[a]; Ludvick O. Urban[a]
[a] Department of Chemistry, Ohio University, Athens, Ohio, U.S.A.

**To cite this Article** Clearfield, Abraham , Gopal, Ramanathan , Kline, Robert J. , Sipski, Marilee and Urban, Ludvick O.(1978) 'THE CRYSTAL STRUCTURE OF trans-AZIDOBIS (ACETYLACETONATO)ETHYLENEDIIMINEPYRI-DINECOBALT(III)', Journal of Coordination Chemistry, 7: 3, 163 — 169

**To link to this Article: DOI:** 10.1080/00958977808073056

**URL:** http://dx.doi.org/10.1080/00958977808073056

*J. Coord. Chem.*
1978, Vol. 7, pp. 163–169

# THE CRYSTAL STRUCTURE OF trans-AZIDOBIS (ACETYLACETONATO)ETHYLENEDIIMINEPYRIDINECOBALT(III)

ABRAHAM CLEARFIELD,[1] RAMANATHAN GOPAL, ROBERT J. KLINE,
MARILEE SIPSKI and LUDVICK O. URBAN

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

*(Received April 13, 1977)*

Crystals of trans-azidobis(acetylacetonato)ethylenediiminepyridine-cobalt(III), $C_{17}H_{23}N_6O_2Co$, are monoclinic with $a = 9.439(9)$, $b = 16.518(13)$, $c = 13.927(7)$ Å and $\beta = 118.95(2)°$. The space group is $P2_1/c$, with $z = 4$. This yields a calculated density ($V = 1898$ Å$^3$) of 1.367 g/cm$^3$ which compares to an observed density of 1.37 g/cm$^3$. Intensity data were obtained with a CAD-4 automated counter diffractometer using the $\theta - 2\theta$ scan technique. The structure was solved by a combination of Patterson and Fourier methods (1854 reflections above background). Refinement by block-diagonal least squares procedures let to a final $R$ of 0.045 and a weighted residual, $Rw$, of 0.039. The cobalt is six coordinate with the BAE ligand occupying the equatorial plane. The chelate rings are non-planar being twisted in opposite directions and folded towards the azide group. The azide group is linear (N–N–N = 176.6) with unequal bond lengths (1.186(8), 1.133(9)). The Co–N–N bond angle is 116.9°. Equatorial Co–N bonds average 1.913(8) Å while the axial Co–N bonds are 1.980(5) Å for pyridine and 1.952(5) for the azide group. All other bond distances and angles are regular. The question of pi interactions in the axial ligands is discussed.

## INTRODUCTION

Six-coordinate cobalt complexes of bis(acetylacetone) ethylenediimine (BAE) and bis(benzoylacetone)ethylenediimine (BBAE) containing dioxygen have been prepared. The compounds $[Co(BAE)PyO_2]$[2] and $[Co(BBAE)PyO_2]$[3] have distorted octahedral structures with the tetradentate ligand occupying equatorial sites and pyridine, (Py), and dioxygen located at the axial positions in the coordination sphere.

The dioxygen is coordinated end-on and has an O–O bond distance typical of a superoxide ligand. Therefore, the cobalt is considered to be Co(III). It is found that the pyridine is necessary to stabilize the complex but there is disagreement as to the nature of the axial interaction between it and the dioxygen group. The role of the pyridine ligand has been ascribed variously as a pi-electron donor,[4] a pi-electron acceptor,[5] or as just a sixth ligand needed to provide enough ligand field strength to stabilize the complex.[6,7]

The pi bonding arguments arise from the finding that the dihedral angle made by the bent Co–O–O group and the plane of the pyridine ring is close to 90° in the complexes above.[2,3] Superoxide ion, pyridine and the metal ion may present orbitals of proper symmetry for pi bonding in this orientation.

It occurred to us that a study of the structure of azido complexes of the type $[Co(BAE)pyN_3]$ could shed some light on the 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 nature of the interaction with the metal centre. Also, the dihedral angle made by the Co–$N_3$ group and the pyridine plane would provide an interesting comparison to the dioxygen complexes.

## EXPERIMENTAL SECTION

Preparation of trans-azidobis(acetylacetonato)ethylenediiminepyridine-cobalt(III). The preparation followed was that given by Bozzeli.[8] 150 ml of ethanol (95%) was boiled for 30 min under a nitrogen atmosphere in a 3-neck round bottom flask fitted with a pressure equalizing separatory funnel. Powdered cobalt(II) acetate 4-hydrate (5.23 g, 21 mmol) was added, followed by a solution of bis(acetylacetonatoethylenediimine) (4.70 g, 21 mmol) and sodium hydroxide (1.68 g, 42.0 mmol) in 80 ml of hot 95% ethanol-water (3:1). Sodium azide (1.37 g, 21.0 mmol), dissolved in 1–2 ml of water, and pyridine (1.6 ml, 21.0 mmol) were added, the mixture was then heated for 10 min, followed by release of the nitrogen atmosphere. The reaction mixture was allowed to cool, with stirring, to room temperature, then transferred to a 500-ml suction flask and aerated for 2.0 hr through a gas dispersion tube and filtered. The filtrate was slowly evaporated to dryness and the recovered solid washed with 150 ml of warm water. Most of the black solid remaining was dissolved in boiling 95% ethanol, then filtered, concentrated and cooled to 0° yielding shiny maroon crystals, 5.9 g (69%); mp 196–197° dec.

Anal. Calcd. for $C_{17}H_{23}CoN_6O_2$: C, 50.74; H, 5.77; N, 20.89. Found: C, 50.89; H, 5.46; N, 20.91.

### *Crystallographic Studies*

The shiny maroon crystals were well-formed air-stable rectangular parallelepipeds. Preliminary survey photographs taken by both the Weissenberg and precession methods revealed a monoclinic unit cell with the following systematic absences: (OkO) for k = 2*n* +1 and (hOℓ) for ℓ = 2*n* +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 0.10 x 0.25 x 0.16 mm. The crystal was mounted with the needle axis (*c* axis) parallel to the axis of the goniometer and slightly offset to avoid doubled reflections. Sets of equivalent reflections were scanned in all octants and their intensities found to agree within 5% in each equivalent set. Fifteen reflections at high and moderate Bragg angles were scanned using a graphite monochromator and 4° take-off angle with Mo $K\alpha_1$ ($\lambda = 0.70926$ Å). The Bragg angles were accurately determined by the use of program DETCELL[9] and unit cell dimensions obtained by least-squares calculations using a locally written program.[10] The results were $a = 9.439(9)$, $b = 16.518(13)$, $c = 13.927(7)$, $\beta = 118.95(2)°$ and $V = 1898.5$ Å$^3$. The density, determined by flotation in an aqueous solution of sodium chloride, was found to be 1.37 g/cm$^3$. This compares to a calculated density with $Z = 4$ and *F.W.* = 402.3, of 1.367 g/cm$^3$.

Intensity data were collected in the $+h$ $+k$ $\pm \ell$ octants out to a maximum Bragg angle of 25°. The $\theta - 2\theta$ scan technique was used with a variable $2\theta$ scan rate given by $(20.1166/X)$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 2.1 to 3.0 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 (0.8 + 0.5 tan $\theta$) deg. Right and left backgrounds were each scanned at 1/4 the total scan time. A total of 3433 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 ±3% overall. The data set was corrected for these fluctuations by assuming a linear change in the intensity of the standards between two consecutive measurements.[11] Only those reflections which gave net counts, determined as NET = TOTAL CTS. – 2(R+L) BKGD. CTS., greater than or equal to $3\sigma$ where $\sigma = (\text{TOTAL CTS.} + \text{BKGRD. CTS.})^{1/2}$ were considered observed. A total of 1854 observed reflections were thus obtained. These were corrected for Lorentz and double polarization effects.[12] No correction for absorption was made since $\mu R$ ($\mu = 9.466$ cm$^{-1}$) ranged from 0.047 to 0.118 and was considered to introduce acceptable errors.

### *Structure Determination and Refinement*

A 3-dimensional Patterson map was prepared from which the peaks of highest density unambiguously gave the coordinates of the cobalt atom. Refinement of the scale factor and the cobalt atom positional parameters with an isotropic temperature factor gave a residual ($R$) of 0.39. Successive Fourier and difference maps yielded the positions of all the non-hydrogen atoms. Least-squares refinement of the positional and isotropic temperature parameters by the block diagonal method,[13] thus reduced the $R$-index to 0.076. Anisotropic refinement, however further lowered the residual index, defined as

$$R = \Sigma(|Fo| - |Fc|) / \Sigma|Fo|, \text{ to } 0.056.$$

Most of the hydrogens were found on electron-density difference synthesis maps at this point with peak heights having minimum and maximum values of about 0.28 and 0.58 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

TABLE I.
Positional parameters and anisotropic thermal parameters ($1 \times 10^4$) for non-hydrogen atoms†

| Atom | x | y | z | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $2\beta_{12}$ | $2\beta_{13}$ | $2\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Co(1) | 0.0538(10) | -0.20848(5) | -0.15248(6) | 101.3(10) | 24.1(3) | 36.7(4) | -7.8(13) | 68.2(12) | -5.7(9) |
| O(1) | 0.1898(4) | -0.2611(2) | -0.1995(3) | 117(7) | 27(2) | 46(3) | 18(5) | 88(8) | 2(4) |
| O(2) | -0.0194(5) | -0.1461(2) | -0.2823(3) | 130(7) | 26(2) | 48(3) | 15(6) | 76(8) | 10(4) |
| N(1) | 0.1247(6) | -0.2736(3) | -0.0243(4) | 167(9) | 32(3) | 42(4) | -26(8) | 89(9) | 4(5) |
| N(2) | -0.0761(6) | -0.1505(3) | -0.1037(4) | 130(9) | 36(2) | 59(4) | -26(8) | 120(10) | -29(5) |
| N(3) | -0.1192(5) | -0.2885(3) | -0.2357(3) | 102(7) | 27(2) | 40(3) | -24(7) | 66(8) | -15(5) |
| N(4) | 0.2249(6) | -0.1304(3) | -0.0680(4) | 122(9) | 31(2) | 64(4) | -25(7) | 93(10) | -19(5) |
| N(5) | 0.3203(6) | -0.1175(3) | -0.0985(4) | 130(9) | 28(2) | 38(4) | -16(7) | 46(9) | -5(5) |
| N(6) | 0.4171(6) | -0.1045(3) | -0.1224(4) | 180(11) | 54(3) | 100(6) | -85(9) | 172(14) | -20(7) |
| C(1) | 0.4196(8) | -0.3240(4) | -0.1838(6) | 167(14) | 46(4) | 125(7) | 61(11) | 186(18) | 16(8) |
| C(2) | 0.3103(7) | -0.3051(4) | -0.1365(5) | 111(9) | 20(3) | 69(5) | -7(8) | 77(11) | -15(6) |
| C(3) | 0.3441(7) | -0.3343(4) | -0.0348(5) | 136(12) | 27(3) | 66(6) | 12(9) | 32(13) | 18(6) |
| C(4) | 0.2477(7) | -0.3211(4) | 0.0163(5) | 137(12) | 28(3) | 43(4) | -41(9) | 13(11) | 0(6) |
| C(5) | 0.2915(10) | -0.3684(5) | 0.1204(6) | 322(20) | 50(4) | 57(6) | 8(15) | 107(18) | 25(8) |
| C(6) | 0.0150(9) | -0.2617(5) | 0.0212(6) | 292(17) | 61(4) | 73(6) | -9(14) | 227(18) | 16(8) |
| C(7) | -0.0413(9) | -0.1774(5) | 0.0060(6) | 255(17) | 56(4) | 82(6) | -6(13) | 209(17) | -17(8) |
| C(8) | -0.2278(9) | -0.0357(5) | -0.0884(7) | 218(16) | 49(4) | 143(8) | -4(12) | 272(20) | -53(9) |
| C(9) | -0.1538(7) | -0.0834(4) | -0.1457(5) | 128(11) | 33(3) | 96(6) | -33(9) | 155(15) | -40(7) |
| C(10) | -0.1799(7) | -0.0542(4) | -0.2470(6) | 139(11) | 27(3) | 96(7) | 24(9) | 103(15) | -1(7) |
| C(11) | -0.1161(7) | -0.0862(4) | -0.3099(5) | 128(11) | 24(3) | 71(5) | -1(9) | 72(13) | 2(6) |
| C(12) | -0.1602(9) | -0.0499(4) | -0.4190(5) | 242(16) | 31(3) | 71(6) | 35(12) | 89(17) | 14(7) |
| C(13) | -0.0828(7) | -0.3665(4) | -0.2337(5) | 113(11) | 34(3) | 58(5) | 3(9) | 63(12) | 5(6) |
| C(14) | -0.1991(7) | -0.4246(4) | -0.2893(5) | 141(12) | 23(3) | 73(6) | 5(9) | 51(14) | -4(6) |
| C(15) | -0.3569(7) | -0.4027(4) | -0.3502(5) | 122(11) | 31(3) | 72(6) | -24(9) | 42(13) | -7(7) |
| C(16) | -0.3950(7) | -0.3224(4) | -0.3534(5) | 101(11) | 37(3) | 63(5) | 8(9) | 45(12) | -9(6) |
| C(17) | -0.2732(7) | -0.2670(4) | -0.2956(5) | 133(11) | 29(3) | 59(5) | -2(9) | 92(12) | -15(6) |

†Thermal parameters in units of $A^2$ are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)] \times 10^4$

TABLE II
Idealized hydrogen atom positional parameters

| Atom | x | y | z |
|---|---|---|---|
| H(1) | -0.2997 | -0.2116 | -0.2964 |
| H(2) | -0.5044 | -0.3031 | -0.3982 |
| H(3) | -0.4406 | -0.4424 | -0.3882 |
| H(4) | -0.1672 | -0.4810 | -0.2859 |
| H(5) | 0.0298 | -0.3817 | -0.1919 |
| H(6) | -0.1361 | -0.1718 | 0.0132 |
| H(7) | 0.0421 | -0.1438 | 0.0599 |
| H(8) | -0.0779 | -0.2986 | -0.0169 |
| H(9) | 0.0676 | -0.2776 | 0.0967 |
| H(10) | 0.4419 | -0.3662 | 0.0041 |
| H(11) | -0.2494 | -0.0077 | -0.2769 |
| H(12) | -0.2500 | -0.0800 | -0.0500 |
| H(13) | -0.2200 | -0.1000 | -0.4800 |
| H(14) | -0.3200 | -0.0100 | -0.1400 |
| H(15) | -0.2149 | -0.0006 | -0.4317 |
| H(16) | -0.2253 | -0.0875 | -0.4750 |
| H(17) | -0.0627 | -0.0396 | -0.4264 |
| H(18) | 0.4700 | -0.2700 | -0.2000 |
| H(19) | 0.5056 | -0.3583 | -0.1359 |
| H(20) | 0.3589 | -0.3524 | -0.2532 |
| H(21) | 0.3800 | -0.4000 | 0.1300 |
| H(22) | 0.2003 | -0.4029 | 0.1115 |
| H(23) | 0.3247 | -0.3336 | 0.1815 |

them. These were included in subsequent structure factor calculations with their coordinates fixed and isotropic thermal parameters set at 6.0 Å$^2$. The final set of agreement parameters was thus obtained: $R = 0.045, R_w = 0.039$, where the weighted $R$-index $(Rw)$[14, 21] is defined as

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

The weighting scheme used in the refinement assigned weights according to the equation $w = 1/[1 + (|Fo| - P_2/P_1)^2]$. $P_1$ and $P_2$ were set at 45 and 98, respectively. The function minimized was $\Sigma w|Fo| - |Fc|)^2$. Neutral atom scattering factors, as listed in the International Tables,[15] were used.

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 exceeding 0.40 eÅ$^3$. The final positional and thermal parameters for the non-hydrogen atoms are given in Table I. Hydrogen atom parameters are presented in Table II. A table of final observed and calculated structure factors may be obtained from the Editor's office.

## *Description of the Structure*

A schematic drawing of the structure with the atom numbering scheme is shown in Figure 1 and the thermal ellipsoids in Figure 2. The bis(acetylacetonato)ethylenediimine dianion (BAE) is found to occupy the equatorial plane, as expected from IR, UV and visible spectrophotometry.[8] Pyridine and azide groups in the axial positions complete the coordination about the cobalt atom.

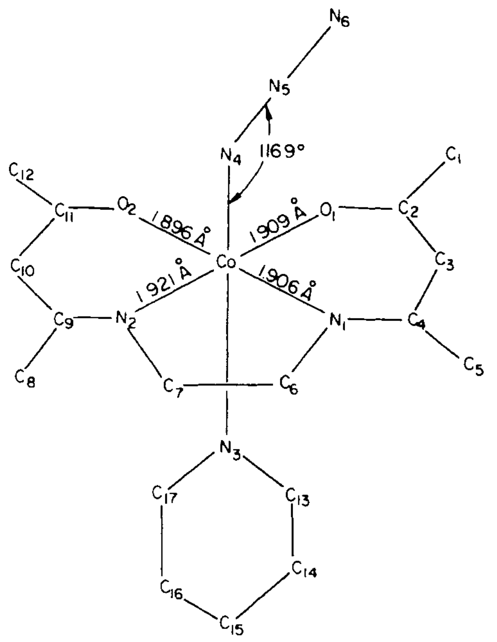

FIGURE 1 Schematic of [Co(BAE)PyN$_3$] showing the numbering system used in the tables.

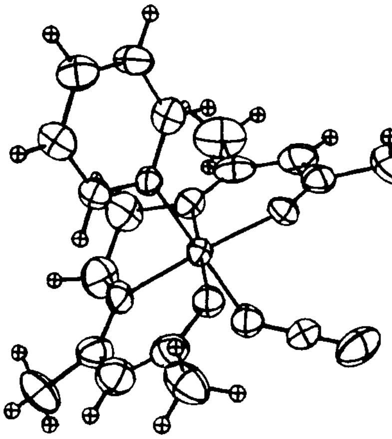

FIGURE 2 A perspective view of [Co(BAE)PyN$_3$] showing the thermal ellipsoids at the 50% probability level.

TABLE III
Interatomic distances (A)

| | | | |
|---|---|---|---|
| Co-O(1) | 1.909(4) | Co-O(2) | 1.896(4) |
| Co-N(1) | 1.906(5) | Co-N(2) | 1.921(5) |
| Co-N(4) | 1.952(5) | Co-N(3) | 1.980(5) |
| N(4)-N(5) | 1.186(8) | N(5)-N(6) | 1.133(9) |
| C(2)-O(1) | 1.274(7) | C(11)-O(2) | 1.273(8) |
| C(4)-N(1) | 1.284(9) | C(9)-N(2) | 1.301(8) |
| C(6)-N(1) | 1.464(11) | C(7)-N(2) | 1.466(9) |
| C(1)-C(2) | 1.501(11) | C(12)-C(11) | 1.492(9) |
| C(2)-C(3) | 1.379(9) | C(11)-C(10) | 1.384(9) |
| C(3)-C(4) | 1.417(10) | C(10)-C(9) | 1.394(9) |
| C(4)-C(5) | 1.516(9) | C(9)-C(8) | 1.511(11) |
| C(6)-C(7) | 1.467(11) | | |
| N(3)-C(13) | 1.330(8) | N(3)-C(17) | 1.326(8) |
| C(13)-C(14) | 1.378(9) | C(17)-C(16) | 1.382(9) |
| C(14)-C(15) | 1.358(10) | C(15)-C(16) | 1.368(9) |

TABLE IV
Interatomic angles (deg)

| | | | |
|---|---|---|---|
| O(1)-Co-O(2) | 85.1(2) | O(1)-Co-N(1) | 94.3(3) |
| O(1)-Co-N(2) | 177.0(2) | O(1)-Co-N(4) | 90.5(2) |
| O(1)-Co-N(3) | 89.8(2) | O(2)-Co-N(2) | 93.8(2) |
| O(2)-Co-N(1) | 178.5(2) | O(2)-Co-N(3) | 89.2(2) |
| O(2)-Co-N(4) | 91.7(2) | N(1)-Co-N(2) | 86.8(2) |
| N(1)-Co-N(3) | 89.4)2) | N(1)-Co-N(4) | 89.7(2) |
| N(2)-Co-N(3) | 93.0(2) | N(2)-Co-N(4) | 86.7(2) |
| N(3)-Co-N(4) | 179.0(2) | | |
| Co-O(1)-C(2) | 123.2(4) | Co-O(2)-C(11) | 125.9(7) |
| Co-N(1)-C(4) | 125.9(6) | Co-N(2)-C(9) | 125.6(6) |
| Co-N(1)-C(6) | 109.0(6) | Co-N(2)-C(7) | 111.3(6) |
| Co-N(4)-N(5) | 116.9(4) | N(4)-N(5)-N(6) | 176.6(6) |
| O(1)-C(2)-C(3) | 126.2(6) | O(2)-C(11)-C(10) | 125.0(6) |
| O(1)-C(2)-C(1) | 113.0(5) | O(2)-C(11)-C(12) | 115.1(6) |
| C(1)-C(2)-C(3) | 120.8(6) | C(12)-C(11)-C(10) | 120.0(6) |
| C(2)-C(3)-C(4) | 125.6(6) | C(11)-C(10)-C(9) | 126.2(6) |
| C(3)-C(4)-C(5) | 117.2(6) | C(10)-C(9)-C(8) | 117.0(6) |
| C(3)-C(4)-N(1) | 122.4(6) | C(10)-C(9)-N(2) | 122.3(8) |
| C(5)-C(4)-N(1) | 120.3(6) | C(8)-C(9)-N(2) | 120.7(8) |
| C(4)-N(1)-C(6) | 124.8(6) | C(9)-N(2)-C(7) | 121.4(6) |
| N(1)-C(6)-C(7) | 110.3(6) | N(2)-C(7)-C(6) | 108.7(6) |
| N(3)-C(13)-C(14) | 122.3(6) | N(3)-C(17)-C(16) | 122.6(6) |
| C(13)-C(14)-C(15) | 120.0(6) | C(17)-C(16)-C(15) | 119.4(6) |
| C(14)-C(15)-C(16) | 118.0(6) | | |

Bond distances and angles are listed in Tables III and IV, respectively. The BAE ring in terms of bond distances is symmetric within the limits of experimental error. Several similar structures (XCo(BAE)L) where X and L are various ligands have appeared in the literature[16,17] and can be used as a basis for comparison (Table V). The cobalt–oxygen and cobalt–nitrogen bond distances of the present compound compare well with those of $C_6H_5Co(BAE)H_2O$ and $CH_2 = CHCo(BAE)H_2O$ as do the other bond distances listed in the Table. While the $C_6$–$C_7$ value for the subject compound is shorter than reported for the other two compounds listed in Table V, it is not significantly so. In any case shorter values for this bond are known.[18] The ligand–cobalt–ligand bond angles in the equatorial plane consist of two which are larger than 90° (N–Co–O) and two smaller (O–Co–O and N–Co–N). Mean plane equations are shown in Table VI. The acetylacetone portions of the BAE ring are significantly non-planar. The two rings twist in opposite directions, O(1) being down toward N(3) while O(2) is up and N(1) is above the plane while N(2) is below it. Single planes drawn through each ring reveals that even the separate acetylacetone segments are non-planar. Also the two halves of the BAE ligand are folded towards the azide group their mean planes making a dihedral angle of

TABLE V
Selected bond distances of atoms in the equatorial plane of some bis(acetylacetonato) cobalt complexes

| | Co-O | Co-N | C-O | C(4)-N Type | C(7)-N Type | C(6)-C(7) |
|---|---|---|---|---|---|---|
| $C_6H_5Co(BAE)H_2O$ | 1.910(10) | 1.890(20) | 1.290(30) | 1.360(30) | 1.500(30) | 1.530(30) |
| $CH_2$ = $CHCo(BAE)H_2O$ | 1.913(7) | 1.888(8) | 1.301(13) | 1.318(13) | 1.476(15) | 1.518(17) |
| | 1.930(7) | 1.892(8) | 1.290(12) | 1.299(13) | 1.466(13) | 1.508(15) |
| Py-Co(BAE)-$N_3$(Avg)[a] | 1.902(6) | 1.913(8) | 1.274(1) | 1.292(8) | 1.465(1) | 1.467(11) |

TABLE VI
Mean planes

A. Chelate Plane

$-0.5522x - 0.6752y - 0.4890z = 2.2384$

$\chi^2 = 33,290$

| | | | |
|---|---|---|---|
| Co | 0.145(1) | C(2) | -0.151(6) |
| O(1) | 0.128(4) | C(3) | -0.230(7) |
| O(2) | 0.122(4) | C(4) | +0.011(6) |
| N(1) | 0.214(5) | C(9) | -0.182(7) |
| N(2) | 0.067(5) | C(10) | -0.144(7) |
| | | C(11) | +0.020(7) |

Other Atoms

| | | | |
|---|---|---|---|
| C(6) | 0.552(8) | C(7) | -0.060(8) |

B. Coordination Plane

$-0.5646x - 0.6528y - 0.5051z = 2.3075$

$\chi^2 = 366$

| | | | |
|---|---|---|---|
| Co | 0.010(1) | N(1) | 0.032(5) |
| O(1) | -0.038(4) | N(2) | -0.037(5) |
| O(2) | 0.033(4) | | |

C. Acetylacetone Ring (O(1), C(2), C(3), C(4), N(1))

$-0.3988x - 0.8075y - 0.4345z = 3.2663$

$\chi^2 = 102$

| | | | |
|---|---|---|---|
| O(1) | 0.018(4) | C(4) | 0.037(6) |
| C(2) | -0.013(6) | N(1) | -0.026(5) |
| C(3) | -0.016(6) | | |

Other Atoms

| | | | |
|---|---|---|---|
| Co | -0.294(1) | N(4) | -2.199 |
| C(1) | -0.049(7) | C(6) | 0.109(8) |
| C(5) | 0.232(7) | C(7) | -0.763(8) |

D. Acetylacetone Ring (O(2), C(11), C(10), C(9), N(2))

$-0.6466x - 0.5747y - 0.5015z = 2.0342$

$\chi^2 = 202$

| | | | |
|---|---|---|---|
| O(2) | -0.035(4) | C(9) | -0.049(7) |
| C(11) | 0.034(7) | N(2) | 0.039(5) |
| C(10) | 0.011(7) | | |

Other Atoms

| | | | |
|---|---|---|---|
| Co | -0.118 | C(6) | 0.320(7) |
| C(8) | -0.151 | C(7) | - .110(7) |
| C(12) | 0.151 | N(4) | -2.05 |

E. Pyridine Ring

$0.5893x + 0.1276y - 0.7978z = 1.9633$

$\chi^2 = 2.6$

| | | | |
|---|---|---|---|
| N(3) | -0.006(4) | C(15) | -0.001(7) |
| C(13) | 0.005(6) | C(16) | +0.000(7) |
| C(14) | -0.002(7) | C(17) | 0.003(6) |

19.9°. This folding is slightly greater than in the N,N′-ethylenebis(1,1,1-trifluoroaceylacetoneiminato) nickel(II) complex.[18] The carbon atoms in the bridging ethylene group (C(6) and C(7)) are in a guache conformation relative to the chelate plane. Even the equatorial coordination at cobalt is nonplanar as the bonded atoms are 0.03–4 Å from the mean plane.

Cobalt–nitrogen bonds in the axial positions are seen to be significantly longer than the cobalt–nitrogen bonds of the equatorial plane. This is not unexpected with ligands of this type and suggests that the axial ligands of this molecule are more labile than the equatorial ones. The cobalt–azide bond distance, 1.952(5) Å, compares to the cobalt–azide distance of 1.957(6) Å found in sym-Co(trenen)$N_3$,[20] and the average distance 1.965(9) in transdiazidoteraammine-cobalt(III) trans-tetraazidodiamminecobaltate(III).[21] Furthermore, the Co–N (Pyridine) distance is almost identical to the Co–N($NH_3$) distances in the cobaltate(III) complex.

The so-called covalent azides are linear and asymmetric possessing unequal N–N distances.[22] This was found to be true in the present structure also. The azide N–N–N bond angle is 176.6(6)°. The bond distance between the nitrogen bonded to the cobalt and the middle nitrogen is 1.187(8) Å while that from the middle nitrogen to the outermost is 1.133(9) Å. As the difference between the two bond lengths is greater than $3\sigma$, where $\sigma = (\sigma_1{}^2 + \sigma_2{}^2)^{1/2}$, this azide is considered to be asymmetric. In all cases where the azide is reported to be asymmetric, the long N–N distance always occurs between the middle nitrogen and the nitrogen coordinated to the metal.[2] These unequal bond lengths are similar to those found in other complexes as may be seen in Table VII. In ionic azides both N–N bonds are of equal length and close to 1.17 Å. Actually, the short N–N bond distance is not very sensitive to the covalency of the M–$N_3$ bond giving values of 1.12–1.15 Å in many structures (Table VII). However, the long N–N bond does vary

TABLE VII
N–N bond distances in some azido compounds

| Compound | Long N-N, Å | Short N-N, Å | References |
|---|---|---|---|
| $N_3^-$ | 1.17 (ave.) | 1.17 (ave.) | 24 |
| $HN_3$ | 1.237 | 1.133 | 25,26 |
| $CH_3N_3$ | 1.24 | 1.12 | 27,28 |
| $[Co(TN)N_3]^{+2}$ | 1.21 | 1.15 | 20 |
| $[Co(NH_3)_5N_3]^{+2}$ | 1.208(7) | 1.145(7) | 29 |
| $[NiNO(PPh_3)_2N_3]$ | 1.22 | 1.12 | 30 |
| $[Zn(NH_3)_2(N_3)_2]$ | 1.18, 1.19 | 1.16, 1.15 | 31 |
| $[Zn(Py)_2(N_3)_2]$ | 1.17, 1.15 | 1.13, 1.13 | 32 |
| $[Ruen_2N_2N_3]^+$ | 1.18 | 1.15 | 33 |
| $[Co(BAE)PyN_3]$ | 1.187(8) | 1.133(9) | This work |
| $[Co(DH)_2PyN_3]$ | 1.158(10) | 1.125(11) | 34 |

Abbreviations: TN = assym-tetraethylenepentamine
Ph = phenyl, Py = pyridine, DH = dimethylglyoximate ion, BAE = bis(acetylacetone)-ethylenediimine ion

with the degree of covalent character of the coordinate bond being 1.24 Å in highly covalent structures and between 1.15 and 1.21 Å in several coordinated metal azides which are partially ionic in nature. In the present case the long N–N distance of 1.187(8) Å signifies some covalent character in the Co–$N_3$ bond. The covalent character is somewhat reduced in $[Co(DH)_2PyN_3]$ judging from the shorter azide N–N distance (Table VII). The dihedral angle between Co–$N_3$ and the pyridine ring plane is 67.8° suggesting a smaller pi interaction than in the dioxygen complex. The azide group almost bisects the $O_1$–$O_2$ distance but is rotated slightly towards O(1). Similarly, the pyridine ring is rotated slightly towards O(1); that is the pyridine ring is rotated such that C(13) is closer to O(1) than N(1). The dimethylglyoxime complex, $[Co(DH)_2PyN_3]$, has an even smaller dihedral angle (26.2°) between the Co–$N_3$ groups and pyridine ring. It should be noted that the complex $[Co(DH)_2PyO_2]$ is not stable; the bridged dimer $[Py(DH)_2Co\text{–}O_2\text{–}Co(DH)_2Py]$ being isolated instead.[35] This could be a consequence of the electron rich nature of the superoxide group in the DH complex which is not relieved by pi delocalization nor, as is suggested by the long N–N distance of 1.158 Å in the azide,[34] by localization in a covalent sigma Co–$N_3$ bond.

The Co–N–N bond angle is 116.9° only slightly lower than usual.[23] The geometry of the pyridine group is regular and mean plane calculations, listed in Table VI, show the ring to be planar.

No intermolecular contacts of less than 3 Å were found and there is no evidence of hydrogen bonding. Thus the crystal consists of independent molecular units of $PyCo(BAE)N_3$. It is possible, however, that crystal packing forces cause the dihedral angles between Co–$N_3$ and the pyridine plane to be other than 90° but more likely that it is due to the folding of the BAE rings. The packing of molecules within the unit cell is illustrated in Figure 3.

In summary, we have found no confirmation of either axial pi bonding theory from the azise study. We have shown, however, that the equatorial ligand is probably as important as the axial one in determining the properties of the dioxygen adducts as is the case with the azides.

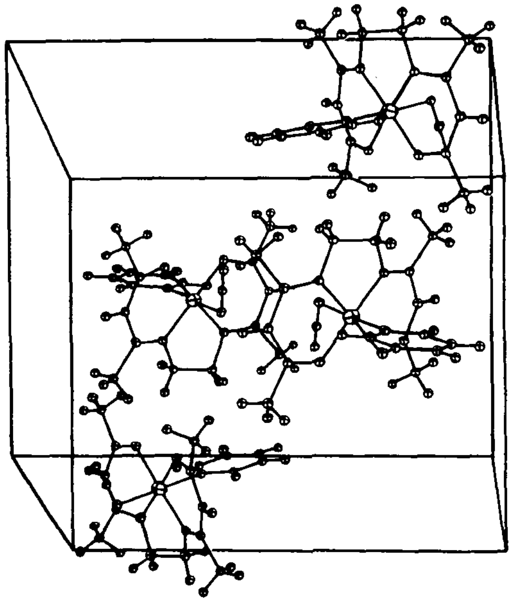

FIGURE 3 Packing diagram of $[Co(BAE)PyN_3]$ unit cell.

## REFERENCES

1. Present address, Dept. of Chem., Texas A&M University, College Station, Texas 77843.
2. M. Calligaris, G. Nardin, L. Randaccio and G. Tauzher, *Inorg. Nucl. Chem. Letters*, 9, 419 (1973).
3. G. A. Rodley and W. T. Robinson, *Nature*, 235, 438 (1972).
4. D. V. Stynes, H. C. Stynes, B. R. James, and J. A. Ibers, *J. Amer. Chem. Soc.*, 95, 1796 (1973).
5. F. A. Walker, *J. Amer. Chem. Soc.*, 95, 1154 (1973).
6. M. J. Carter, D. P. Rillema and F. Basolo, *J. Amer. Chem. Soc.*, 96, 392 (1974).
7. C. J. Weschler, D. L. Anderson and F. Basolo, *Chem. Commun.*, 757 (1974).
8. J. W. Bozzeli, *Master's Thesis*, Ohio University, December 1972.
9. Enraf-Nonius, *Instruction Manual for CAD-4 System*, Delft, Holland (1972).

10. G. D. Smith, Cell Dimensions–Least Squares Program, Ohio University Crystallography Laboratory, Athens, Ohio (1968).
11. R. W. Olson, CAD-4 Output Tape Process, Ohio University Crystallography Laboratory, Athens, Ohio (1973).
12. U. W. Arndt and B. T. M. Willis, *Single Crystal Diffractometry,* Cambridge University Press, (1966), p. 286.
13. The programs used for structure solution and refinement were those of F. R. Ahmed, S. R. Hall, M. E. Pippy and C. P. Huber, *NRC Crystallographic Programs for the IBM-360,* National Research Council, Ottawa, Canada, 1968.
14. W. C. Hamilton, *Acta. Cryst.,* **18**, 502 (1965).
15. J. A. Ibers, *International Tables for X-ray Crystallography,* Vol. III, Kynoch Press, Birmingham (1962), pp. 202–203.
16. S. Bruckner, M. Calligaris, G. Nardin and L. Randaccio, *Chem. Commun.,* **152** (1970).
17. S. Bruckner, M. Calligaris, G. Nardin and L. Randaccio, *Inorg. Chem., Acta,* **2**, 416 (1968).
18. R. P. Scaringe and D. J. Hodgson, *Inorg. Chem.,* **15**, 1193 (1976).
19. T. M. Calligaris, D. Minichelli, G. Nardin and L. Randaccio, *J. Chem. Soc.* **(A)**, 2411 (1970).
20. I. E. Maxwell, *Inorg. Chem.,* **10**, 1782 (1971).
21. L. F. Druding, F. D. Sancilio and D. M. Lukaszewski, *Inorg. Chem.,* **14**, 1365 (1975).
22. N. Muller, *Z. Anorg. Allg. Chem.,* **382**, 110 (1971).
23. Z. Dori and R. F. Zilio, *Chem. Rev.,* 73, 247 (1973).
24. U. Muller, *Z. Anorg. Allg. Chem.,* **392**, 159 (1972).
25. E. Amble and B. P. Dailey, *J. Chem. Phys.,* **18**, 1437 (1950).
26. M. Winnewesser and R. L. Cook, *J. Chem. Phys.,* **41**, 999 (1964).
27. L. Pauling and L. O. Brockway, *J. Amer. Chem. Soc.,* **59**, 13 (1937).
28. R. L. Livingston and C. N. R. Rao, *J. Chem. Phys.,* **64**, 756 (1960).
29. G. J. Palenik, *Acta. Cryst.,* **17**, 360 (1964).
30. J. H. Ennemark, *Inorg. Chem.,* **10**, 1952 (1971).
31. I. Agrell and N. G. Vannerberg, *Acta. Chem. Scand.,* **25**, 1630 (1971).
32. I. Agrell and N. G. Vannerberg, *Acta. Chem. Scand.,* **24**, 1247 (1970).
33. B. R. Davis and J. A. Ibers, *Inorg. Chem.,* **9**, 2768 (1970).
34. *J. Coord. Chem.,* to be submitted.
35. G. N. Schrauzer and R. J. Windgassen, *Chem. Ber.,* **99**, 602 (1966).