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(13) The identity of this species as a dibromo derivative, rather than as a monobromomonochloro derivative was checked very carefully. (i) Elemental analysis of this sample is as follows (cf. ref 6). Anal. Calcd for the empirical formula $C_7H_{26}B_5Br_2IrOP_2$: C, 14.15; H, 4.42; B, 9.09; Br, 26.89; Ir, 32.34; P, 10.50. Found: C, 14.09; H, 4.39; B, 8.84; Br, 26.88; Ir, 35.45; P, 10.50. (ii) Based on the unit cell volume, the calculated density is 2.036 g cm^{-3} for the dibromo derivative and 1.884 g cm^{-3} for the monobromomonochloro derivative. We measured the density by "neutral buoyancy" in three different solutions, obtaining the following values: 2.014 g cm^{-3} for aqueous $ZnBr_2$, 2.015 g cm^{-3} for $C_2H_2Br_4$–CCl_4, and 2.008 g cm^{-3} for $C_2H_2Br_4$–$C_2H_4Cl_2$. The mean of these three values is 2.012 g cm^{-3}. Assuming *no* errors, this is consistent with there being a mixture of 84.2% dibromo and 15.8% monobromomonochloro complex. (iii) The behavior of the bromine atoms under least-squares refinement is reasonable. Br(1) is further distant from the iridium atom and has a higher thermal parameter than does B(2). An opposite effect would be expected if one atomic position were a composite "bromine–chlorine" atom. The centroid would then be closer to iridium that a normal bromine, and the thermal parameter should be higher than normal, reflecting (a) disorder about two atomic centers (a normal Cl position and a normal Br position) and (b) an electron count less than that expected for a pure bromine atom. We conclude, therefore, that, if the sample is contaminated by chloride, it is at a lower level than we can detect from an X-ray study.
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Determination of the Crystal Structure and Molecular Geometry of [Hydrotris(1-pyrazolyl)borato]copper(I) Carbonyl. A Unique Structural Investigation of a Copper–Carbonyl Linkage

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The species [hydridotris(1-pyrazolyl)borato]copper(I) carbonyl, $[HB(C_3N_2H_3)_3]Cu(CO)$, crystallizes in the noncentrosymmetric rhombohedral space group $R3c$ [C_{3v}^6; No. 161] with $a = 13.8616\ (21)$ Å and $\alpha = 91.37\ (1)°$. The observed density is 1.45 (5) g cm^{-3}; that calculated for mol wt 304.58, $V = 2661.1\ (12)$ Å^3, and $Z = 8$ is 1.520 g cm^{-3}. Single-crystal X-ray diffraction data were collected on a Picker FACS-1 automated diffractometer using a θ–2θ scan. The structure was solved by a combination of Patterson, Fourier, and least-squares refinement techniques. All atoms were located, the final discrepancy indices being $R_F = 2.85\%$ and $R_{wF} = 3.20\%$ for the 1726 symmetry-independent reflections representing data complete to $2\theta = 45°$ (Mo Kα radiation). The crystallographic asymmetric unit contains one and one-third molecules of $[HB(C_3N_2H_3)_3]Cu(CO)$ and there are thus two crystallographically distinct types of molecule within the unit cell. One type of molecule has precise (i.e., crystallographically dictated) C_3 symmetry, while the other has no symmetry and is, in fact, somewhat distorted from the C_{3v} symmetry which the molecule could possess. The two independently determined copper(I)–carbonyl bond lengths are 1.755 (11) and 1.775 (5) Å [average 1.765 ± 0.014 Å]. Other bond distances fall into the following ranges: Cu–N = 2.039 (4)–2.059 (3) Å, C–O = 1.120 (6) and 1.120 (13) Å, N–N = 1.350 (5)–1.378 (5) Å, N–C = 1.331 (7)–1.361 (6) Å, C–C = 1.354 (8)–1.386 (8) Å, and N–B = 1.526 (6)–1.558 (6) Å. For the molecule lying on the crystallographic C_3 axis, bond angles around the copper(I) atom are C(1)–Cu(1)–N(11) = 124.4 (1)° and N(11)–Cu(1)–N(11′) = 91.3 (2)°. For the molecule lying in the general position, OC–Cu–N angles range from 119.4 (2) to 127.3 (2)° and N–Cu–N angles are 90.4 (1)–92.4 (2)°.

Introduction

Binary carbonyls, $M_x(CO)_y$, are known for each of the first-row transition elements from vanadium through nickel. There is, however, no stable (i.e., isolable under ambient conditions) binary carbonyl of copper, although evidence has accumulated for the existence of such species under extreme conditions, viz., as a short-lived intermediate following the passage of halogen-free carbon monoxide over heated copper,[3] as a surface species in chemisorption of carbon monoxide on metallic copper,[4,5] and as a product from the condensation of hot copper atoms onto a carbon monoxide matrix at 20°K.[6]

Carbonyl *complexes* of copper are confined to the copper(I) oxidation state. These species have been under investigation for some time.[7] Thus, in 1850 Leblanc[8a] showed that am-

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Table I. Experimental Data for the X-Ray Diffraction Study of $(HB(pz)_3)Cu(CO)$

(A) Crystal Parameters (at 21.0°)[a]

Crystal system: rhombohedral	Space group: $R3c$
$a = 13.8616\ (21)$ Å	$Z = 8$
$\cos \alpha = -0.0237\ (2)$	Mol wt 304.58
$\alpha = 91.37\ (1)°$	$\rho(\text{calcd}) = 1.520$ g cm^{-3}
$V = 2661.1\ (12)$ Å^3	$\rho(\text{obsd}) = 1.45\ (5)^b$ g cm^{-3}

(B) Measurement of Intensity Data

Radiation: Mo Kα
Filter(s): Nb foil at counter aperture (~47% transmission of Mo Kα)
Attenuators: not used (see text)
Takeoff angle: 3.0°
Detector aperture: 6.3 × 6.3 mm
Crystal–detector distance: 330 mm
Crystal orientation: ϕ axis = $[\bar{1}11]$
Reflections measured: one quadrant of the reciprocal sphere
Maximum 2θ: 45°
Scan type: coupled θ(crystal)–2θ(counter)
Scan speed: 1.0°/min
Scan length: $\Delta(2\theta) = (0.90 + 0.692 \tan \theta)°$, starting 0.45° below the Mo Kα_1 peak
Background measurement: stationary crystal, stationary counter; 20 sec each at beginning and end of 2θ scan
Standard reflections: three remeasured after every 48 reflections; rms deviations (after application of an isotropic linear decay correction)[d] were 1.58% for 004, 0.51% for $23\bar{2}$, and 1.11% for $\bar{2}2\bar{3}$
Reflections collected: 1726 independent measurements, 1770 duplicate or equivalent measurements (averaged into primary data set), and 224 systematic absences; the agreement between equivalent reflections, $R(F^2)$, was 3.4%

(C) Treatment of Intensity Data

Conversion to $|F_o|$ and $\sigma|F_o|$: as in ref 21, using an "ignorance factor" of $p = 0.04$
Absorption coefficient: $\mu = 17.05$ cm^{-1}; no absorption corrections applied

[a] Unit cell parameters are from a least-squares fit to the setting angles of the resolved Mo Kα_1 peaks (λ 0.709300 Å[c]) of 12 reflections ($2\theta = 40$–46°). [b] Neutral buoyancy in saturated KI. This value is not very reliable, due to decomposition product on the surface of the crystals. [c] J. A. Bearden, *Rev. Mod. Phys.*, 39, 78 (1967). [d] Data reduction was performed using the Fortran IV program RDUS, by B. G. DeBoer.

Table II. Final Positional Parameters,[a] with Esd's[b] for $[HB(C_3N_2H_3)_3]Cu(CO)$

Atom	x	y	z	B,[c] Å^2
		(A) Molecule 1 (on C_3 axis)[d]		
Cu(1)[e]	1/4	$=x$	$=x$	4.33
C(1)[e]	0.3249 (4)	$=x$	$=x$	5.51
O(1)[e]	0.3727 (4)	$=x$	$=x$	10.42
B(1)[e]	0.1208 (4)	$=x$	$=x$	3.40
N(11)	0.1433 (3)	0.2987 (3)	0.1601 (3)	3.89
N(12)	0.0916 (3)	0.2271 (3)	0.1134 (2)	3.38
C(11)	0.0998 (4)	0.3814 (4)	0.1375 (4)	4.37
C(12)	0.0207 (4)	0.3623 (4)	0.0775 (4)	5.13
C(13)	0.0170 (3)	0.2644 (4)	0.0645 (3)	4.06
H(1)[e]	0.0725	$=x$	$=x$	4.22
H(11)	0.1209	0.4433	0.1616	4.73
H(12)	−0.0224	0.4068	0.0498	5.15
H(13)	−0.0292	0.2284	0.0260	4.34
		(B) Molecule 2 (in General Position)		
Cu(2)	0.23416 (5)	0.48246 (6)	0.63940 (5)	3.76
C(2)	0.3158 (3)	0.5426 (4)	0.5630 (4)	4.83
O(2)	0.3638 (3)	0.5834 (4)	0.5135 (4)	8.82
B(2)	0.0877 (3)	0.3979 (4)	0.7739 (4)	3.47
N(21)	0.2678 (2)	0.3960 (2)	0.7535 (2)	3.15
N(22)	0.1910 (2)	0.3665 (2)	0.8046 (2)	2.88
C(21)	0.3446 (3)	0.3576 (3)	0.7970 (3)	3.62
C(22)	0.3176 (3)	0.3028 (3)	0.8745 (3)	4.10
C(23)	0.2186 (3)	0.3100 (3)	0.8770 (3)	3.60
N(23)	0.1455 (3)	0.5616 (2)	0.7239 (3)	3.84
N(24)	0.0875 (3)	0.5089 (2)	0.7804 (3)	3.45
C(24)	0.1354 (4)	0.6544 (4)	0.7522 (4)	5.13
C(25)	0.0711 (4)	0.6600 (4)	0.8266 (4)	5.88
C(26)	0.0430 (4)	0.5678 (4)	0.8446 (4)	5.16
N(25)	0.1246 (3)	0.3891 (3)	0.5966 (3)	3.59
N(26)	0.0667 (2)	0.3609 (2)	0.6708 (2)	3.16
C(27)	0.0922 (4)	0.3396 (4)	0.5186 (4)	4.43
C(28)	0.0139 (4)	0.2806 (4)	0.5400 (4)	5.29
C(29)	0.0022 (3)	0.2955 (3)	0.6359 (4)	4.31
H(2)	0.0371	0.3569	0.8176	3.94
H(21)	0.4084	0.3676	0.7749	4.00
H(22)	0.3573	0.2681	0.9178	4.42
H(23)	0.1785	0.2802	0.9229	3.78
H(24)	0.1702	0.7055	0.7232	5.26
H(25)	0.0505	0.7163	0.8599	5.96
H(26)	−0.0011	0.5508	0.8931	5.26
H(27)	0.1199	0.3461	0.4569	4.98
H(28)	−0.0221	0.2371	0.4982	5.66
H(29)	−0.0472	0.2651	0.6715	4.68

[a] Using rhombohedral (*not* hexagonal) coordinates. [b] Esd's are right-adjusted to the last digit of the preceding number and are those derived from the inverse of the final least-squares matrix. [c] For the full anisotropic thermal parameters of nonhydrogen atoms, see Table III. [d] Only the coordinates for atoms in the asymmetric unit are given. For the coordinates of the other atoms in this molecule use the cyclic transformations $[x', y', z'] = [y, z, x]$ and $[x'', y'', z''] = [z, x, y]$. [e] These atoms lie on the crystallographic C_3 axis.

moniacal cuprous chloride solution dissolved carbon monoxide until a 1:1 Cu:CO ratio was reached. Manchot and Friend[8b] subsequently showed the product of this reaction to be $Cu(CO)Cl(H_2O)_2$. The literature on the absorption of CO by copper(I) salts was covered comprehensively by Gmelin.[9]

The analogous anhydrous chlorocarbonyl species Cu(CO)Cl, originally reported by Hieber et al.,[10] is now believed to be $[Cu(CO)Cl]_2$.[11]

Recently prepared molecular copper(I) carbonyl species, all of which are unstable, include $(CF_3CO_2)Cu(CO)$,[12] $(\pi\text{-}C_5H_5)Cu(CO)$,[13] $[Cu(en)(CO)]Cl$ (en = $NH_2CH_2CH_2NH_2$),[14] $[(en)Cu(CO)_2Cu(en)]Cl_2$,[14] $[Cu(CO)Cl(Me_2N{=}CH_2)^+]$,[15] and a hemocyanin–carbon monoxide adduct.[16] A copper(I) carbonyl species has also been detected in Y zeolite.[17]

The only *stable* copper(I) carbonyl complexes are the poly(pyrazolyl)borate species synthesized by Bruce et al. The parent species $[HB(C_3N_2H_3)_3]Cu(CO)$, hereafter referred to as $(HB(pz)_3)Cu(CO)$, was reported in 1972;[18] various substituted derivatives were synthesized later.[19]

We now report the results of a single-crystal X-ray diffraction study of $(HB(pz)_3)Cu(CO)$. To our knowledge, this is the first reported structural study on a copper–carbonyl derivative.

Collection of the X-Ray Diffraction Data

The complex $(HB(pz)_3)Cu(CO)$ was prepared as described previously.[18] The crystals thus obtained were globular and rather greasy in appearance and were coated with a bluish green powder, believed to be a product of decomposition.[20] The crystal selected for the diffraction study had no well-defined faces and a rather irregular geometry which approximated to an ellipsoid of dimensions (radii, along principal axes) ~0.3 mm × ~0.1 mm × ~0.1 mm.

As much decomposition product as possible was scraped from the crystal's surface and the crystal was placed in a thin-walled capillary tube which was then flushed with nitrogen, flame-sealed, fixed in a brass pin, and mounted on a eucentric goniometer.

Preliminary precession and cone-axis photographs yielded approximate cell dimensions, indicated $\bar{3}m$ (D_{3d}) Laue symmetry, and exhibited the systematic absences hhl for $l = 2n + 1$ (only); these data are consistent with the rhombohedral space groups $R3c$ (C_{3v}^6; No. 161) and $R\bar{3}c$ (D_{3d}^6; No. 167). The former, noncentrosymmetric space group is required in the absence of gross disorder and was confirmed by the successful solution of the structure. With $Z = 8$, one set of six molecules will occupy general positions, while a second set of two molecules will occupy positions of precise (crystallographic) C_3 (3) point symmetry.

Table III. Anisotropic Thermal Parameters[a] for $[HB(C_3N_2H_3)_3]Cu(CO)$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	$\langle U\rangle$[b]
				(A) Molecule 1			
Cu(1)	4.29 (2)	$=B_{11}$	$=B_{11}$	−0.69 (2)	$=B_{12}$	$=B_{12}$	0.19, 0.25, 0.25
C(1)	5.47 (20)	$=B_{11}$	$=B_{11}$	−0.69 (25)	$=B_{12}$	$=B_{12}$	0.22, 0.28, 0.28
O(1)	10.26 (29)	$=B_{11}$	$=B_{11}$	−3.16 (28)	$=B_{12}$	$=B_{12}$	0.22, 0.42, 0.42
B(1)	3.38 (15)	$=B_{11}$	$=B_{11}$	−0.33 (16)	$=B_{12}$	$=B_{12}$	0.18, 0.22, 0.22
N(11)	4.57 (18)	2.99 (17)	4.06 (18)	0.03 (14)	−0.38 (15)	−0.15 (13)	0.19, 0.22, 0.25
N(12)	3.45 (16)	3.68 (17)	3.01 (15)	0.06 (13)	−0.26 (12)	0.18 (13)	0.19, 0.21, 0.22
C(11)	5.05 (26)	3.67 (22)	4.41 (24)	0.16 (19)	0.83 (19)	−0.44 (18)	0.20, 0.23, 0.26
C(12)	5.54 (28)	5.60 (30)	4.47 (24)	2.04 (23)	1.48 (21)	1.42 (21)	0.21, 0.22, 0.32
C(13)	3.47 (20)	5.53 (27)	3.22 (19)	0.20 (17)	0.40 (15)	0.77 (17)	0.19, 0.21, 0.27
				(B) Molecule 2			
Cu(2)	3.29 (3)	3.85 (3)	4.20 (3)	−0.13 (2)	0.50 (2)	1.14 (2)	0.18, 0.21, 0.25
C(2)	3.80 (23)	6.02 (28)	4.71 (23)	−0.68 (20)	−0.06 (20)	1.84 (21)	0.20, 0.22, 0.30
O(2)	6.47 (24)	11.89 (36)	8.12 (28)	−3.86 (23)	0.47 (22)	4.55 (27)	0.19, 0.31, 0.45
B(2)	2.30 (19)	3.92 (23)	4.20 (24)	−0.01 (16)	−0.15 (16)	0.73 (18)	0.17, 0.21, 0.24
N(21)	2.33 (14)	3.20 (15)	3.93 (16)	−0.12 (11)	0.10 (12)	0.74 (12)	0.17, 0.19, 0.23
N(22)	2.20 (14)	2.99 (14)	3.48 (16)	−0.09 (11)	0.32 (12)	0.48 (12)	0.16, 0.19, 0.22
C(21)	2.38 (17)	3.65 (19)	4.89 (23)	0.50 (15)	0.11 (15)	0.86 (17)	0.17, 0.21, 0.26
C(22)	3.60 (21)	4.35 (21)	4.39 (22)	0.74 (17)	−0.56 (16)	0.99 (18)	0.18, 0.24, 0.26
C(23)	3.81 (21)	3.67 (20)	3.35 (20)	0.02 (15)	0.26 (15)	0.40 (16)	0.20, 0.22, 0.22
N(23)	3.75 (17)	2.71 (16)	5.06 (19)	0.22 (13)	−0.33 (15)	0.17 (14)	0.18, 0.22, 0.26
N(24)	2.89 (15)	3.63 (17)	3.81 (16)	0.72 (13)	−0.24 (13)	−0.47 (14)	0.18, 0.20, 0.24
C(24)	4.72 (26)	4.22 (26)	6.33 (30)	0.22 (19)	−2.01 (23)	−0.65 (21)	0.20, 0.23, 0.32
C(25)	6.15 (30)	4.33 (29)	7.04 (34)	1.61 (23)	−1.32 (26)	−2.32 (23)	0.19, 0.25, 0.35
C(26)	4.11 (23)	6.64 (32)	4.71 (25)	1.98 (22)	−0.61 (18)	−1.64 (21)	0.20, 0.22, 0.33
N(25)	3.48 (16)	3.71 (16)	3.59 (17)	0.18 (13)	−0.16 (13)	0.31 (13)	0.20, 0.22, 0.22
N(26)	2.59 (14)	3.25 (15)	3.64 (17)	0.04 (12)	−0.09 (12)	0.08 (12)	0.18, 0.20, 0.22
C(27)	5.38 (26)	4.45 (23)	3.45 (21)	0.88 (20)	−0.50 (18)	−0.22 (17)	0.20, 0.22, 0.28
C(28)	5.24 (26)	4.90 (25)	5.60 (30)	−0.02 (22)	−1.28 (21)	−1.06 (21)	0.21, 0.26, 0.30
C(29)	3.25 (21)	4.34 (22)	5.28 (26)	−0.40 (16)	−0.44 (18)	−0.11 (18)	0.19, 0.24, 0.26

[a] These anisotropic thermal parameters are analogous to the usual form of the isotropic thermal parameters and have units of Å². They enter the expression for the structure factor in the form $\exp[-\frac{1}{4}a^{*2}(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$. [b] These values correspond to the root-mean-square amplitudes of vibration (in Å) of the atom along the three principal axes (minor, median, major, respectively) of its vibrational ellipsoid. For relative orientations, see the figures.

The crystal was transferred to a Picker FACS-1 computer-controlled diffractometer, was centered such that the center of gravity of the crystal was coincident with the diffractometer's "sphere of confusion", and was oriented such that [$\bar{1}$11] was coincident with the instrumental ϕ axis. As a check on possible variations in transmission factor, the strong axial $\bar{2}$22 reflection was measured, by a θ–2θ scan, at χ = 90° and at 10° intervals from ϕ = 0° to ϕ = 360°. The maximum variation from the mean was ~5%, suggesting that absorption was not a severe problem. (The possibility of an analytical absorption correction was negated by the irregular shape of the crystal.)

Data collection was carried out as described previously;[21] details of the present study are given in Table I.

It should be noted that the only reflections with an intensity greater than 10^4 counts/sec were at $2\theta < 10°$. In order to avoid coincidence losses (and in the absence of automatic insertion of attenuators—a diffractometer feature which was malfunctioning during the course of data collection), data with $2\theta < 10°$ were collected at a tube current of 2 mA and then of 16 mA. The scale factor between the data sets was determined by comparing the reflections in the range of linearity (i.e., up to 10^4 counts/sec); values for the stronger reflections were taken from the (scaled) 2-mA data only.

Solution and Refinement of the Structure

All calculations were performed on an IBM 370/158 computer. Programs used included FORDAP (Fourier synthesis, by A. Zalkin), LSHF (structure factor calculations and least-squares refinement, by B. G. DeBoer), STANI (distances and angles, with esd's, by B. G. DeBoer), PLOD (least-squares planes and lines, by B. G. DeBoer), and ORTEP (thermal ellipsoid drawings, by C. K. Johnson).

Scattering factors for neutral copper, oxygen, nitrogen, carbon, and boron were taken from the compilation of Cromer and Waber;[22] the values for the real and imaginary components of anomalous dispersion for these atoms were taken from the listing of Cromer and Liberman.[23] For hydrogen atoms, the scattering curve of Stewart et al. was used.[24]

The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = [\sigma(|F_o|)]^{-2}$. Discrepancy indices used below are defined as

$$R_F = \left[\frac{\Sigma ||F_o| - |F_c||}{\Sigma |F_o|}\right] \times 100\ (\%)$$

$$R_{wF} = \left[\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w |F_o|^2}\right]^{1/2} \times 100\ (\%)$$

A three-dimensional Patterson synthesis, based on 1726 independent reflections, was solved on the basis of the noncentrosymmetric space group $R3c$. The crystallographic asymmetric unit consists of one and one-third molecules of $[HB(C_3N_2H_3)_3]Cu(CO)$.

The origin of the unit cell was fixed by assigning the coordinates 0.25, 0.25, 0.25 to atom Cu(1) (the copper atom associated with the molecule lying on the crystallographic threefold axis).

The two crystallographically independent copper atoms were used to phase a three-dimensional Fourier synthesis, from which the positions of 20 of the 26 remaining nonhydrogen atoms were identified. A second Fourier synthesis, now phased by these additional atoms, quickly revealed the locations of the remaining nonhydrogen atoms. Several cycles of full-matrix least-squares refinement, first with isotropic thermal parameters and then with anisotropic thermal parameters for all nonhydrogen atoms, led to convergence (Δ/σ = 0.002 being the largest shift in the final cycle) with R_F = 2.85% and R_{wF} = 3.20% for all 1726 independent reflections (none rejected).

During the later cycles of refinement, hydrogen atoms were included in the calculation. Each was assigned an isotropic thermal parameter 1.0 Å² greater than the value for its bonded carbon or boron atom at the termination of isotropic refinement. The positions of the pyrazolyl hydrogens were defined 0.95 Å[25] outward along the (centroid of pyrazolyl ring)→(carbon atom) vectors. The positions of the boron-bonded hydrogen atoms were calculated as 1.0 Å from boron, in the direction of the sum of the three associated nitrogen-to-boron (unit) vectors. Each [C–H] and [B–H] system was treated as a rigid nonrotating group. Also, during the last few cycles of refinement, a secondary extinction parameter was included as a variable (following

Table IV. Interatomic Distances (Å) and Their Esd's[a]

Molecule 1		Molecule 2	
	A. Copper-Nitrogen		
Cu(1)-N(11)	2.048 (4)	Cu(2)-N(21)	2.059 (3)
		Cu(2)-N(23)	2.039 (4)
		Cu(2)-N(25)	2.039 (4)
	B. Copper-Carbonyl and Carbon-Oxygen		
Cu(1)-C(1)	1.755 (11)	Cu(2)-C(2)	1.775 (5)
C(1)-O(1)	1.120 (13)	C(2)-O(2)	1.120 (6)
	C. Nitrogen-Nitrogen		
N(11)-N(12)	1.353 (6)	N(21)-N(22)	1.353 (4)
		N(23)-N(24)	1.350 (5)
		N(25)-N(26)	1.378 (5)
	D. Nitrogen-Carbon		
N(11)-C(11)	1.348 (6)	N(21)-C(21)	1.339 (5)
N(12)-C(13)	1.343 (6)	N(22)-C(23)	1.342 (5)
		N(23)-C(24)	1.347 (6)
		N(24)-C(26)	1.361 (6)
		N(25)-C(27)	1.331 (7)
		N(26)-C(29)	1.332 (6)
	E. Carbon-Carbon		
C(11)-C(12)	1.378 (8)	C(21)-C(22)	1.384 (6)
C(12)-C(13)	1.364 (8)	C(22)-C(23)	1.380 (6)
		C(24)-C(25)	1.382 (7)
		C(25)-C(26)	1.358 (8)
		C(27)-C(28)	1.386 (8)
		C(28)-C(29)	1.354 (8)
	F. Boron-Nitrogen		
B(1)-N(12)	1.542 (5)	B(2)-N(22)	1.558 (6)
		B(2)-N(24)	1.540 (6)
		B(2)-N(26)	1.526 (6)

[a] Esd's, shown in parentheses, are right-adjusted to the last digit of the preceding number. They are calculated from the full positional correlation matrix using the Fortran IV program STAN1 by B. G. DeBoer. Contributions from errors in the unit cell parameters are included. No distances have been corrected for possible librational effects.

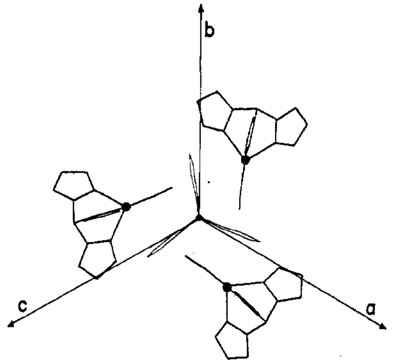

Figure 1. Packing of molecules within the unit cell, as viewed down [111]. Half of the unit cell contents is shown.

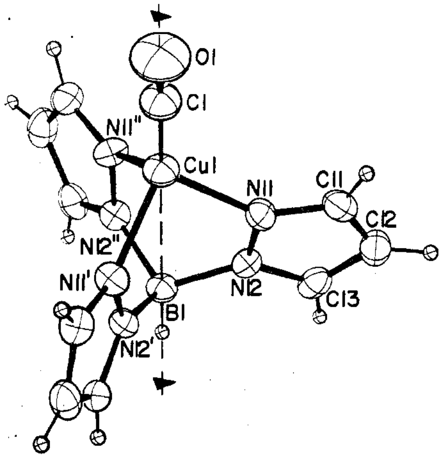

Figure 2. Geometry and numbering of molecule 1, which lies on the crystallographic C_3 axis (ORTEP diagram with 50% probability envelopes for the thermal ellipsoids). [Hydrogen atoms are shown, artificially reduced, as spheres of radius 0.1 Å.]

the observation that the five most intense reflections had $|F_o| < |F_c|$). The final value for the secondary extinction parameter (c) was 2.06 (15) × 10^{-5} e^{-2}. This parameter enters the equation for the corrected structure factor ($F_{c,cor}$) in the form[26,27]

$$F_{c,cor} = F_{c,uncor}(1 + c\beta F^2_{c,uncor})^{-1/4}$$

where, in the absence of the calculation of any transmission factors, β was assigned a value of unity for all reflections.

The final standard deviation of an observation of unit weight, otherwise termed the "goodness of fit", defined by the expression $[\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, was 1.18 where m (the number of observations) was 1726 and n (the number of variables) was 229. The data to parameter ratio (n:m) is 7.54:1. The function $\sum w(|F_o| - |F_c|)^2$ was not appreciably dependent either upon $(\sin\theta)/\lambda$ or upon $|F_o|$, thereby indicating a correctly chosen weighting scheme. A final difference-Fourier synthesis showed, as its highest feature, a peak of height 0.26 e Å^{-3}. The correctness and completeness of the structural analysis are therefore independently confirmed.

Since the space group $R3c$ is noncentrosymmetric (even though it contains an operation of the second kind), we tested the chirality *of the particular crystal investigated* by transforming all coordinates (x, y, z) to ($-x, -y, -z$). Refinement to convergence resulted in the increased residuals R_F = 4.26% and R_{wF} = 5.69%. The original choice of handedness was thus correct. These later results were discarded.

A table of observed and calculated structure factor amplitudes is available.[28]

Final positional and isotropic thermal parameters are collected in Table II; anisotropic thermal parameters are listed in Table III.

Discussion of the Molecular Structure

Interatomic distances and their estimated standard deviations (esd's) are given in Table IV; bond angles and their esd's are collected in Table V.

The crystal consists of discrete molecular units of (HB(pz)$_3$)Cu(CO) which are mutually separated by normal van der Waals distances. The packing of molecules within the unit cell is illustrated in Figure 1. The crystallographic asymmetric unit consists of one and one-third molecules; there are, therefore, two crystallographically distinct molecules within the unit cell. Molecule 1 has precise (i.e., crystallographically dictated) C_3 (3) symmetry with atoms O(1), C(1), Cu(1), B(1), and H(1) lying along the [111] direction. Molecule 2 is in a general position and has no crystallographic symmetry imposed upon it. The presence of two crystallographically unrelated molecules in the asymmetric unit provides an excellent test of internal consistency of molecular parameters (particularly bond *lengths*) and also shows the magnitude of the perturbations than can be caused by packing forces (typically angular deformations).

The scheme used in numbering atoms is such that the first digit of the atom number identifies the molecule to which the atom belongs. The numbering schemes for molecules 1 and 2 are displayed in Figures 2 and 3, respectively.

The hydrotris(1-pyrazolyl)borate anion acts as a tridentate ligand and donates six electrons to the d^{10} copper(I) atom; the carbonyl ligand donates two electrons, thereby completing the (distorted) tetrahedral arrangement of donor ligands around the central atom and also completing the 18-outer-electron ("noble gas") configuration of this atom.

The two independent copper-carbonyl bond lengths are Cu(1)-C(1) = 1.755 (11) Å and Cu(2)-C(2) = 1.775 (5) Å; the average value is 1.765 ± 0.014 Å.[29] The two C-O distances are C(1)-O(1) = 1.120 (13) Å and C(2)-O(2) = 1.120 (6) Å. While these values are lower than the normal terminal C-O distance of ca. 1.14-1.16 Å in transition metal carbonyls, we

Table V. Interatomic Angles (deg)[a]

Molecule 1		Molecule 2	
A. Oxygen–(Carbonyl Carbon)–Copper			
O(1)–C(1)–Cu(1)	180.0 (–)	O(2)–C(2)–Cu(2)	176.6 (5)
B. (Carbonyl Carbon)–Copper–Nitrogen			
C(1)–Cu(1)–N(11)	124.4 (1)	C(2)–Cu(2)–N(21)	127.3 (2)
		C(2)–Cu(2)–N(23)	119.4 (2)
		C(2)–Cu(2)–N(25)	126.4 (2)
C. Nitrogen–Copper–Nitrogen			
N(11)–Cu(1)–N(11′)	91.3 (2)	N(21)–Cu(2)–N(23)	90.8 (1)
		N(21)–Cu(2)–N(25)	90.4 (1)
		N(23)–Cu(2)–N(25)	92.4 (2)
D. Copper–Nitrogen–Nitrogen			
Cu(1)–N(11)–N(12)	113.6 (3)	Cu(2)–N(21)–N(22)	114.5 (2)
		Cu(2)–N(23)–N(24)	114.6 (2)
		Cu(2)–N(25)–N(26)	113.7 (3)
E. Copper–Nitrogen–Carbon			
Cu(1)–N(11)–C(11)	140.0 (4)	Cu(2)–N(21)–C(21)	140.1 (3)
		Cu(2)–N(23)–C(24)	138.4 (4)
		Cu(2)–N(25)–C(27)	140.2 (4)
F. Nitrogen–Nitrogen–Carbon			
N(12)–N(11)–C(11)	106.0 (4)	N(22)–N(21)–C(21)	105.4 (3)
N(11)–N(12)–C(13)	109.8 (4)	N(21)–N(22)–C(23)	110.9 (3)
		N(24)–N(23)–C(24)	106.1 (4)
		N(23)–N(24)–C(26)	110.0 (4)
		N(26)–N(25)–C(27)	106.0 (4)
		N(25)–N(26)–C(29)	108.4 (4)
G. Nitrogen–Carbon–Carbon			
N(11)–C(11)–C(12)	110.3 (5)	N(21)–C(21)–C(22)	111.2 (4)
N(12)–C(13)–C(12)	108.6 (5)	N(22)–C(23)–C(22)	107.8 (4)
		N(23)–C(24)–C(25)	110.0 (5)
		N(24)–C(26)–C(25)	107.6 (5)
		N(25)–C(27)–C(28)	111.0 (4)
		N(26)–C(29)–C(28)	110.4 (4)
H. Carbon–Carbon–Carbon			
C(11)–C(12)–C(13)	105.3 (4)	C(21)–C(22)–C(23)	104.7 (4)
		C(24)–C(25)–C(26)	106.2 (4)
		C(27)–C(28)–C(29)	104.3 (5)
I. Boron–Nitrogen–Nitrogen			
B(1)–N(12)–N(11)	121.0 (4)	B(2)–N(22)–N(21)	119.7 (3)
		B(2)–N(24)–N(23)	120.3 (3)
		B(2)–N(26)–N(25)	120.5 (3)
J. Nitrogen–Boron–Nitrogen			
N(12)–B(1)–N(12′)	108.3 (4)	N(22)–B(2)–N(24)	107.1 (4)
		N(22)–B(2)–N(26)	108.3 (4)
		N(24)–B(2)–N(26)	111.3 (3)
K. Boron–Nitrogen–Carbon			
B(1)–N(12)–C(13)	129.2 (5)	B(2)–N(22)–C(23)	129.4 (3)
		B(2)–N(24)–C(26)	129.3 (4)
		B(2)–N(26)–C(29)	130.9 (4)

[a] See footnote *a* to Table IV.

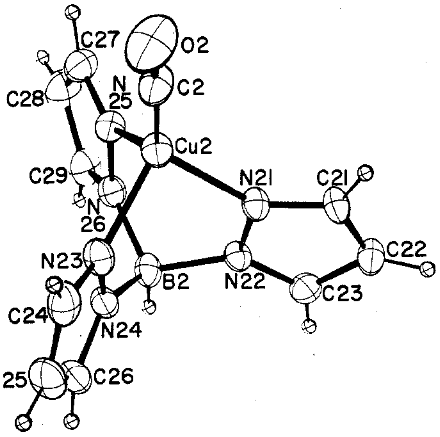

Figure 3. Geometry and numbering of molecule 2. Conditions are as for Figure 2.

Table VI

Least-Squares Lines and Planes[a–c]

Atom	Dev, Å	Atom	Dev, Å
Line 1: $X = 0.5770T + 3.612$, $Y = 0.5635T + 3.527$, $Z = 0.5912T + 3.700$			
Cu(1)*	0.000	O(1)*	0.000
C(1)*	0.000	B(1)*	0.000
Line 2: $X = 0.6646T + 3.260$, $Y = 0.4318T + 6.666$, $Z = -0.6098T + 8.623$			
Cu(2)*	0.099	O(2)*	0.074
C(2)*	0.032	B(2)*	0.054
Plane 1: $-0.5951X - 0.0928Y + 0.7983Z = 0.242$			
N(11)*	0.004	Cu(1)	0.204
N(12)*	−0.006	B(1)	−0.026
C(11)*	−0.000		
C(12)*	−0.003		
C(13)*	0.006		
Plane 2a: $0.0931X + 0.7920Y + 0.6034Z = 10.707$			
N(21)*	−0.005	C(23)*	−0.003
N(22)*	0.005	Cu(2)	−0.010
C(21)*	0.003	B(2)	−0.005
C(22)*	−0.000		
Plane 2b: $0.7436X - 0.1154Y + 0.6586Z = 7.054$			
N(23)*	0.004	C(26)*	0.010
N(24)*	−0.009	Cu(2)	0.295
C(24)*	0.002	B(2)	0.114
C(25)*	−0.008		
Plane 2c: $-0.6215X + 0.7561Y - 0.2050Z = 1.254$			
N(25)*	0.000	C(29)*	−0.008
N(26)*	0.005	Cu(2)	−0.114
C(27)*	−0.005	B(2)	−0.090
C(28)*	0.008		

Angles between the Lines and Planes

Angle	Value, deg	Angle	Value, deg
Line 1–plane 1	4.4	Plane 2a–plane 2b	112.0
Line 2–plane 2a	2.1	Plane 2a–plane 2c	114.7
Line 2–plane 2b	2.4	Plane 2b–plane 2c	133.2
Line 2–plane 2c	2.2		

[a] All calculations were performed using the Fortran IV program PLOD, by B. G. DeBoer. [b] Equations to planes and lines are presented in cartesian (Å) coordinates such that X, Y, and Z lie in the directions ($b \times c^*$), b, and c^*, respectively. [c] Atoms identified by an asterisk were assigned unit weights; all others were given zero weight.

emphasize that no bond lengths have been corrected for possible librational shortening (see Table IV and Figures 2 and 3 for details of the rather large thermal ellipsoids associated with atoms of the carbonyl groups).

The Cu(1)–C(1)–O(1) system is precisely linear, while ∠Cu(2)–C(2)–O(2) is 176.6 (5)°. We note here that, since the molecule contains only one carbonyl group and the *idealized* molecular symmetry is C_{3v}, the metal–carbonyl systems are expected to be precisely linear;[30] any statistically significant deviation from linearity can then result only from crystal-packing forces.

The four independent Cu–N(pyrazolyl) linkages range from 2.039 (4) to 2.059 (3) Å, the mean value being 2.046 ± 0.010 Å. [Since the covalent radius of sp^3-hybridized nitrogen is identical with that for sp-hybridized carbon (i.e., 0.70 Å), this suggests that a Cu(I)–C(sp) bond of unit bond order would be approximately 2.05 Å and that the present Cu–CO bonds are contracted from normal single-bond lengths by ca. 0.28 Å.]

The intramolecular N–Cu–N angles are all significantly less than the ideal tetrahedral angle of 109.5°, due to a combination of the constraints within the hydrotris(1-pyrazolyl)borate ligand

and the requirements for normal copper–nitrogen bond distances. Individual values range from N(21)–Cu(2)–N(25) = 90.4 (1)° to N(23)–Cu(2)–N(25) = 92.4 (2)°. This necessarily affects the N(pyrazolyl)–Cu–C(carbonyl) angles, all of which are considerably greater than the ideal tetrahedral angle and range from 119.4 (2) to 127.3 (2)°.

An isolated (HB(pz)$_3$)Cu(CO) molecule is expected to possess precise C_{3v} symmetry. In the present study of the *solid-state* geometry, we find that neither molecule has symmetry this high. Thus, although molecule 1 has crystallographically imposed C_3 symmetry, the pyrazolyl groups each make an angle of 4.4° with the line defined by atoms Cu(1), C(1), O(1), and B(1). The slightly propeller-like conformation of this molecule is shown in Figure 1. (For details of least-squares lines and planes, see Table VI.)

The distortions of molecule 2 from C_{3v} symmetry are considerably more pronounced and can be recognized and defined by the following data.

(1) Irregularities in the OC–Cu(2)–N angles: thus, C(2)–Cu(2)–N(23) = 119.4 (2)°, C(2)–Cu(2)–N(25) = 126.4 (2)°, and C(2)–Cu(2)–N(21) = 127.3 (2)°.

(2) Irregularities in the angles between the planes that define the pyrazolyl systems (see Table VI): thus, dihedral angles are plane 2a–plane 2b = 112.0°, plane 2a–plane 2c = 114.7°, and plane 2b–plane 2c = 133.2°.

(3) Nonlinearity of the B(2)···Cu(2)–C(2)–O(2) system: as shown in Table VI, deviations of atoms from the least-squares line defined by these four atoms are 0.099 Å for Cu(2), 0.074 Å for O(2), 0.054 Å for B(2), and 0.032 Å for C(2).

We note here that distortions are also found in (HB(pz)$_3$)$_2$Co.[31] Here, the major distortion from (the idealized) D_{3d} symmetry appears to involve slight rotations of the pyrazolyl rings about their appropriate N(1)–N(2) axes, resulting in the angles between adjacent [viewed down the S_6 axis] pyrazolyl ligands ranging from 52° 5' to 76° 25'.

Bond lengths within the four crystallographically independent pyrazolyl systems are self-consistent. The N–N distances range from 1.350 (5) to 1.378 (5) Å, averaging 1.358 ± 0.013 Å;[29] C–N distances vary from N(25)–C(27) = 1.331 (7) Å to N(24)–C(26) = 1.361 (6) Å, the average of the eight independent values being 1.343 ± 0.010 Å; C–C distances again show little variation, individual measurements ranging from C(28)–C(29) = 1.354 (8) Å to C(27)–C(28) = 1.386 (8) Å and averaging 1.373 ± 0.013 Å.

Each of the pyrazolyl rings is planar within the limits of experimental error, *maximum* deviations from planarity being 0.006 Å for plane 1, 0.005 Å for plane 2a, 0.010 Å for plane 2b, and 0.008 Å for plane 2c.

The copper atoms are *not* coplanar with the pyrazolyl rings. Thus, Cu(1) is displaced by 0.204 Å from the plane defined by N(11), N(12), C(11), C(12), and C(13) [and, of course, by an identical distance from the two symmetry-related pyrazolyl rings in this molecule]. Similarly Cu(2) is displaced by 0.295 Å from plane 2b, by 0.114 Å from plane 2c, but by only 0.010 Å from plane 2a.

The boron atom is also displaced from the planes of the pyrazolyl rings, although by lesser amounts than the copper atom—viz., by 0.114 Å from plane 2b, by 0.090 Å from plane 2b, and by only 0.005 Å from plane 2a (see Table VI).

The four independent B–N distances range from 1.526 (6) to 1.558 (6) Å, the average of these values being 1.542 ± 0.013 Å (cf. 1.544 ± 0.021 Å in (HB(pz)$_3$)$_2$Co[31]).

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Registry No. [HB($C_3N_2H_3$)$_3$]Cu(CO), 52374-64-8.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number AIC406836-9-75.

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