Preparation and Crystal and Molecular Structure of Dibromo(1,4,7-triazacyclononane)copper(II)

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The preparation, spectroscopic properties, and crystal structure are reported for a monomeric copper(II) compound containing the cyclic triamine 1,4,7-triazacyclononane ([9]aneN$_3$). The compound Cu([9]aneN$_3$)Br$_2$ is isolated by the slow evaporation of a basic aqueous solution of equimolar concentrations of CuBr$_2$ and the triamine. Optical and electron spin resonance spectra do not differentiate between the various coordination environments possible for the copper(II) ion. The bright green compound crystallizes in the centrosymmetric space group $P\bar{1}$ with a = 7.0309 (10) Å, b = 7.6230 (11) Å, c = 10.2406 (15) Å, α = 86.610 (12)°, β = 76.371 (11)°, γ = 77.272 (11)°, and V = 520.3 Å^3. The observed density was 2.28 g/cm^3 whereas the calculated density was 2.25 g/cm^3 for mol wt 352.54 and Z = 2. Diffraction data were collected with a Syntex $P2_1$ automated diffractometer using graphite-monochromatized Mo Kα radiation. The positions of the copper and two bromine atoms were located on a Patterson synthesis, and all other nonhydrogen atoms were located in subsequent difference Fourier syntheses. Hydrogen atoms were placed in idealized positions. Final discrepancy indices are R_F = 4.41% and R_{wF} = 4.07% for all 1844 symmetry independent reflections in the range 4° ≤ 2θ ≤ 45° (none rejected). The copper atom is five-coordinate with the cyclic triamine occupying two equatorial sites and the one axial site of a distorted square pyramid. The copper atom is raised slightly from the basal plane toward the axial nitrogen atom. The axial Cu–N distance of 2.231 (4) Å is typically longer than the equatorial Cu–N distances (2.047 (4) and 2.046 (4) Å). Bond distances and angles within the coordinated triamine suggest it is a rather *rigid* ligand. A discussion of the significance of this geometry when compared with other potential structures is presented.

Introduction

Our chemical and spectral investigations of copper(II)-containing metalloproteins have led us to attempt to design and prepare small molecules which might mimic aspects of the enzyme metal center.[1-4] With this in mind, we have begun to consider copper(II) complexes with tridentate ligands in the hope that the remaining coordination sites would be available either for substitution reactions or for a systematic variation and study of ligand types. One aspect of this problem, the knowledge that type I copper(II) in proteins has either a *pseudo*tetrahedral geometry or at least a C_3 axis,[5,6] led us to consider the coordination chemistry of rigid tridentate ligands.

A good deal of recent work has appeared on the coordination chemistry of cyclic triamines.[7-14] Zompa and co-workers have reported that a 1:1 complex between ([9]aneN$_3$) (**1a**) and Cu(II) should be stable on the basis of potentiometric titrations[7] but were unable to isolate any 1:1 product from subsequent reactions. Both copper(II) and nickel(II) complexes of this ligand with 2:1 ligand to metal stoichiometries have been isolated.[7] Zompa and Margulis[9] have recently reported the crystal structure of Ni([9]aneN$_3$)$_2$NO$_3$Cl·H$_2$O. The dimeric copper(II) complexes of [Cu(p,q,r-cy)Cl]ClO$_4$ (see **1b**) have been reported,[10] and apparently each copper
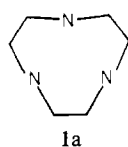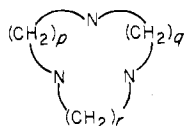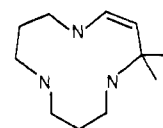
atom is five-coordinate with bridging chlorine atoms. To date, only one example of a copper(II) monomeric complex with a cyclic triamine has been reported; Curtis and co-workers[14] have recently reported the isolation of the Cu(II) complex of the cyclic triamine represented as **1c**. That complex has the same stoichiometry, Cu(**1c**)(SCN)$_2$, as that reported here.

We now report the preparation and study of Cu([9]-aneN$_3$)Br$_2$. Since spectroscopic data did not differentiate between the various coordination possibilities for this complex, we also report a crystal and molecular structural study for this

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1c

complex. In addition, we suggest a possible explanation for the geometry adopted by the copper(II).

Experimental Section

Materials. All reagents and solvents were reagent grade.

1,4,7-Triazocyclononane Trihydrobromide. Richman's modification[15] of the procedure of Koyama and Yoshino[16] was employed for the preparation of this compound. A satisfactory elemental analysis was obtained.

Dibromo(1,4,7-triazacyclononane)copper(II). A solution consisting of 0.372 g (1 mmol) of 1,4,7-triazacyclononane trihydrobromide in 4 mL of water was added to a solution of 0.223 g (1 mmol) of copper(II) bromide in 5 mL of water. Air was bubbled through this dark blue solution for 5 min, after which 0.1 g of sodium hydroxide was added. The resulting solution was allowed to evaporate slowly in air to near dryness. The fine green crystals which precipitated were collected by filtration and recrystallized from a small amount of water.

An elemental analysis, obtained from Galbraith Laboratories, Knoxville, TN, was in agreement with the formulation above. Anal. Calcd for Cu(C$_6$N$_3$H$_{15}$)Br$_2$: C, 20.42; H, 4.25; N, 11.91; Br, 45.38. Found: C, 20.50; H, 4.32; N, 11.85; Br, 45.19.

Spectroscopic Measurements. Optical spectra were obtained as Nujol mulls and dimethyl sulfoxide and aqueous solutions with a Cary 14 spectrophotometer. Electron spin resonance spectra in a dimethyl sulfoxide frozen solution were obtained as before.[1]

Crystal Structure Determination. The crystal used in the diffraction experiment was an irregularly shaped cube measuring approximately 0.20 mm on an edge. The crystal was jammed into a 0.2-mm thin-walled glass capillary which was sealed and fixed with beeswax in an aluminum pin on a eucentric goniometer head.

This was fixed to the goniostat, and the crystal was centered in the X-ray beam of a Syntex $P2_1$ four-circle diffractometer under control of a Data General Nova 1200 computer with 24K of 16-bit word memory and a Diablo disk unit of 1.2 million 16-bit words. The relative orientation and unit cell parameters of the crystal were determined, and the X-ray data were collected by methods described previously.[17] The crystal was found to possess triclinic symmetry. The centrosymmetric space group $P\bar{1}$ was confirmed by successful refinement of the structure. Specifics of the data collection are given in Table I.

1a

1b: p, q, r = 2–6

Table I. Data for the X-ray Diffraction Study of Cu([9]aneN$_3$)Br$_2$

(A) Crystal Data

cryst system: triclinic	$V = 520.3$ Å^3
space group: $P\bar{1}$	$T = 25 \pm 1$ °C
$a = 7.0309$ (10) Å	$Z = 2$
$b = 7.6230$ (10) Å	mol wt 352.6
$c = 10.2406$ (15) Å	ρ(obsd) = 2.28 g/cm^3 ^{a}
$\alpha = 86.610$ (12)°	ρ(calcd) = 2.25 g/cm^3
$\beta = 76.371$ (11)°	
$\gamma = 77.272$ (11)°	

(B) Intensity Data

radiation: Mo Kα
monochromator: highly oriented graphite
rflcns measd: $h,\pm k,\pm l$
max 2θ: 50°
min 2θ: 4°
scan type: θ–2θ
scan speed: 4°/min
scan range: sym [1.8 + Δ(α_2–α_1)]°
rflcns collected: 1844
abs coeff: 102.6 cm^{-1}, empirical abs cor made

^{a} Measured by neutral buoyancy in aqueous ZnI$_2$.

Solution and Refinement of the Structure

Initial calculations through the generation of a Patterson synthesis were performed by using the Syntex XTL structure determination system, including the aforementioned computing hardware and a locally modified version of the XTL conversational crystallographic program package. Subsequent difference Fourier syntheses and structure refinement were carried out on the CDC 6600/CYBER 173 computer at the State University of New York at Buffalo. Programs other than those in the Syntex XTL structure determination system included TAPRE (reads nine-track, ASCII-character string magnetic tape created by the program CDCOUT of the XTL system and converts the tapes read to coded files), LSHF (structure factor calculations and full-matrix least-squares refinement, by B. G. DeBoer), JIMDAP (Fourier synthesis, derived from the program FORDAP by A. Zalkin), STANI (by B. G. DeBoer: calculates angles and distances between atom positions), PLOD (least-squares planes), HAITCH (calculates atomic positions from geometric consideration; employed here to calculate H atom positions), FTABL (prints tables of integerized F_o's, F_c's, and $\sigma(F_o)$'s), and ORTEP (thermal ellipsoid plotting program).

Scattering factors for neutral copper, bromine, nitrogen, and carbon were taken from the compilation of Cromer and Waber;[18] for hydrogen, the "best floated spherical H atom" values of Stewart et al.[19] were used. Both the real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion were included for all nonhydrogen atoms by using the values of Cromer and Liberman.[20]

The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = [\sigma(|F_o|)]^{-2}$. Discrepancy indices used in the text are defined in eq 1 and 2. The "goodness of fit" (GOF) is defined by eq 3, wherein NO is the number of observations and NV is the number of variables.

$$R_F = \left[\frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \right] \times 100 \ (\%) \tag{1}$$

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

$$\text{GOF} = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\text{NO} - \text{NV}} \right]^{1/2} \tag{3}$$

Normalized structure factor amplitudes, $|E(hkl)|$, were generated from $|F_o(hkl)|$ values by using eq 4. Here the summation is over

$$|E(hkl)| = |F_o(hkl)|[\epsilon \sum_{j=1}^{j=N} f^2[j,\theta(hkl)]]^{-1/2} \tag{4}$$

all N atoms in the unit cell, $\langle|E(khl)|^2\rangle$ is normalized by a scale factor, $f[j,\theta(hkl)]$ is the scattering factor for the jth atom at the Bragg angle $\theta(hkl)$, and ϵ is a coefficient which corrects for the effects of space

Table II. Positional Parameters and Their Standard Deviations for Cu([9]aneN$_3$)Br$_2$

atom	x	y	z
Br(1)	1.03605 (8)	0.63512 (7)	0.81767 (5)
Br(2)	0.61205 (9)	0.77085 (7)	0.67717 (6)
Cu	0.77886 (9)	0.49579 (8)	0.76906 (6)
N(1)	0.5368 (6)	0.3842 (6)	0.7771 (4)
N(2)	0.9200 (7)	0.3110 (6)	0.5955 (4)
N(3)	0.8658 (6)	0.2694 (6)	0.8763 (4)
C(1)	0.5697 (8)	0.2714 (7)	0.6566 (5)
C(2)	0.7414 (9)	0.3058 (8)	0.5446 (5)
C(3)	1.0123 (9)	0.1372 (7)	0.6503 (6)
C(4)	1.0475 (9)	0.1618 (8)	0.7883 (6)
C(5)	0.7019 (9)	0.1691 (7)	0.9238 (5)
C(6)	0.5054 (9)	0.2833 (8)	0.9049 (5)
H(N1)	0.4195 (6)	0.4733 (6)	0.7748 (4)
H(N2)	1.0249 (7)	0.3443 (6)	0.5285 (4)
H(N3)	0.8948 (6)	0.3000 (6)	0.9570 (4)
H1(C1)	0.6008 (8)	0.1487 (7)	0.6828 (5)
H2(C1)	0.4503 (8)	0.2940 (7)	0.6244 (5)
H1(C2)	0.6990 (9)	0.4185 (8)	0.5041 (5)
H2(C2)	0.7756 (9)	0.2135 (8)	0.4795 (5)
H1(C3)	1.1357 (9)	0.0880 (7)	0.5904 (6)
H2(C3)	0.9234 (9)	0.0575 (7)	0.6582 (6)
H1(C4)	1.1549 (9)	0.2221 (8)	0.7779 (6)
H2(C4)	1.0817 (9)	0.0472 (8)	0.8287 (6)
H1(C5)	0.6918 (9)	0.1385 (7)	1.0161 (5)
H2(C5)	0.7322 (9)	0.0625 (7)	0.8726 (5)
H1(C6)	0.4519 (8)	0.3657 (8)	0.9772 (5)
H2(C6)	0.4140 (8)	0.2085 (8)	0.9041 (5)
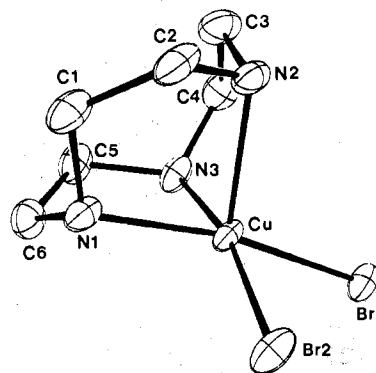
Figure 1. Molecular geometry and labeling of atoms in the Cu(N$_3$C$_6$H$_{15}$)Br$_2$ molecule (H's not included) (ORTEP-II diagram, 30% probability ellipsoids).

group symmetry. The statistical distribution of $|E|$ values was in keeping with that expected for a centrosymmetric crystal.

The positions of the copper and bromine atoms were determined from a Patterson synthesis. Subsequent least-squares refinement and difference Fourier maps allowed all remaining carbon and nitrogen atoms to be located. Positions of the hydrogen atoms were calculated, constrained in their associated carbon or nitrogen atom, and included in the final least-squares refinement.

Final discrepancy indices were R_F = 4.41% and R_{wF} = 4.07%, and the "goodness of fit" was 1.627. There was evidence for secondary extinction, and refinement of the secondary extinction parameter yielded $c = 3.526 \times 10^{-5}$.[21] There were no identifiable features on the final difference Fourier map.

A table of observed and calculated structure factor amplitudes is available (supplementary material). Positional parameters are collected in Table II; thermal parameters are listed in Table III.

Results and Discussion

Interatomic distances and their estimated standard deviations (esd's) are listed in Table IV. Bond angles and their esd's are given in Table V. An ORTEP diagram of the molecule is shown in Figure 1.

Optical spectral features (in cm^{-1} × 10^3 (numbers in parentheses are molar absorptivities)) [mull, 14.8, 23.5, 28.6; H$_2$O, 9.30 (13.0), 15.3 (39.5), 39.3 (265); Me$_2$SO, 9.05 (27.9), 15.0 (153), 36.1 (691)] as well as observed electron spin

Table III. Thermal Parameters and Their Standard Deviations for Cu([9]aneN$_3$)Br$_2$

(A) Anisotropic Parameters[a]

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br(1)	3.016 (26)	2.837 (26)	3.225 (26)	−1.333 (19)	−1.169 (19)	0.435 (18)
Br(2)	3.657 (28)	1.953 (24)	4.168 (29)	−0.682 (19)	−1.585 (21)	0.906 (19)
Cu	2.231 (27)	1.671 (26)	2.061 (26)	−0.606 (20)	−0.558 (20)	0.270 (18)
N(1)	2.12 (17)	1.99 (18)	2.77 (19)	−0.56 (14)	−0.67 (14)	0.31 (14)
N(2)	2.82 (19)	2.25 (19)	2.51 (18)	−0.45 (16)	0.13 (15)	0.15 (14)
N(3)	3.05 (20)	2.60 (20)	2.77 (19)	−0.96 (16)	−1.40 (16)	0.63 (15)
C(1)	3.56 (26)	2.66 (24)	3.29 (25)	−0.90 (21)	−1.81 (21)	0.41 (19)
C(2)	4.99 (31)	2.73 (24)	2.13 (22)	−1.04 (22)	−1.08 (21)	−0.06 (18)
C(3)	2.67 (23)	2.52 (25)	3.73 (26)	0.01 (19)	0.08 (20)	−0.26 (19)
C(4)	3.11 (26)	2.32 (24)	5.76 (34)	−0.46 (20)	−1.91 (25)	0.77 (22)
C(5)	4.13 (27)	2.43 (23)	2.54 (22)	−1.29 (21)	−1.03 (20)	0.96 (18)
C(6)	3.23 (25)	3.20 (25)	2.70 (23)	−1.45 (21)	−0.27 (19)	0.50 (19)

(B) Isotropic Thermal Parameters[b]

atom	B_{iso}, Å^2	atom	B_{iso}, Å^2
H(N1)	3.18	H1(C2), H2(C2)	4.13
H(N2)	3.60	H1(C3), H2(C3)	4.08
H(N3)	3.57	H1(C4), H2(C4)	4.48
H1(C1), H2(C2)	3.84	H1(C5), H2(C5)	3.85
		H1(C6), H2(C6)	3.98

[a] The anisotropic thermal parameter is defined by the expression $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}ha^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. [b] Isotropic thermal parameters are given for hydrogen atoms. These are based on the *isotopic* thermal parameters of the attached carbon or nitrogen atom: $B(H_i) = B(C_i \text{ or } N_i) + 1.0$ (Å^2).

Table IV. Bond Distances (Å) for Cu(N$_3$C$_6$H$_{15}$)Br$_2$

(A) Bond Distances within Metal Coordination Sphere

Cu-Br(1)	2.4453 (8)	Cu-N(2)	2.230 (4)
Cu-Br(2)	2.4209 (8)	Cu-N(3)	2.046 (4)
Cu-N(1)	2.047 (4)		

(B) Bond Distances within Ligand (N-C)

N(1)-C(1)	1.490 (7)	N(2)-C(3)	1.482 (7)
N(1)-C(6)	1.474 (6)	N(3)-C(4)	1.483 (7)
N(2)-C(2)	1.478 (7)	N(3)-C(5)	1.493 (7)

(C) Bond Distances within Ligand (C-C)

C(1)-C(2)	1.514 (8)	C(5)-C(6)	1.510 (8)
C(3)-C(4)	1.521 (8)		

Table V. Bond Angles (deg) for Cu(N$_3$C$_6$H$_{15}$)Br$_2$

(A) Angles within CuN$_3$Br$_2$ Core

Br(1)-Cu-Br(2)	93.26 (3)	Br(2)-Cu-N(2)	106.05 (12)
Br(1)-Cu-N(1)	166.22 (12)	Br(2)-Cu-N(3)	168.17 (13)
Br(1)-Cu-N(2)	108.26 (12)	N(1)-Cu-N(2)	83.47 (16)
Br(1)-Cu-N(3)	91.92 (12)	N(2)-Cu-N(3)	82.33 (17)
Br(2)-Cu-N(1)	90.24 (12)	N(3)-Cu-N(1)	82.32 (17)

(B) Angles with N at the Vertex

Cu-N(1)-C(1)	110.59 (31)	Cu-N(2)-C(3)	107.15 (31)
Cu-N(1)-C(6)	106.75 (31)	Cu-N(3)-C(4)	106.29 (32)
Cu-N(2)-C(2)	99.93 (30)	Cu-N(3)-C(5)	112.27 (32)
C(6)-N(1)-C(1)	113.55 (41)	C(4)-N(3)-C(5)	113.48 (43)
C(2)-N(2)-C(3)	114.26 (44)		

(C) Angles with C at the Vertex

N(1)-C(1)-C(2)	112.94 (43)	N(2)-C(3)-C(4)	110.90 (44)
N(1)-C(6)-C(5)	110.10 (42)	N(3)-C(4)-C(3)	111.02 (44)
N(2)-C(2)-C(1)	111.66 (41)	N(3)-C(5)-C(6)	110.03 (41)

resonance parameters in Me$_2$SO ($A_{\parallel}$ = 148.5 G, $A_{\perp}$ = 29.6 G, A_0 = 59.0 G, $g_{\parallel}$ = 2.278, $g_{\perp}$ = 2.050, g_0 = 2.126) are not those expected for a pseudotetrahedral geometry[6] and also do not define the coordination environment. The crystal structure of ([9]aneN$_3$)CuBr$_2$ clearly indicates that the cyclic triamine occupies three sites on one triangular face of a square pyramid, with the two remaining equatorial sites occupied by the two Br atoms.

Despite recent advances and clarifications of bonding theories for transition-metal complexes, it is still difficult to predict with any degree of certainty when a five-coordinate species will form or what stereochemistry it will adopt.[22]
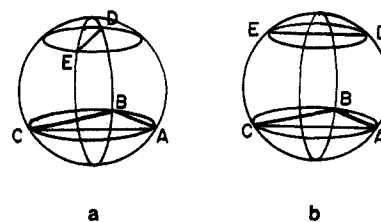

a　　　　　**b**

Figure 2. The two idealized limiting geometries for a rigid tridentate and two monodentate ligands forming a five-coordinate complex. (See ref 29 in relation to geometry b.)

Clearly, the size of the coordinated metal atom, as well as the sizes and shapes of the ligands will have a major influence on the coordination number and stereochemistry of a complex within the two idealized five-coordinate geometries, trigonal bipyramidal and square pyramidal. Various researchers have addressed the problem of the *relative* stabilities of these two idealized structures with little success.[23-28]

Kepert,[29] however, has developed a relatively useful and accurate method for predicting the stereochemistry of complexes consisting of a central metal surrounded by various ligand environments. His method involves the minimization of the ligand repulsive energy within the coordinate framework based on potential-energy surface considerations. The specific case of five-coordination, involving one rigid[29] tridentate ligand and two monodentate ligands (the exact situation for the copper(II) complex here), is treated in detail by Kepert. Kepert's approach could have predicted, a priori, the same general stereochemistry exhibited by Cu([9]aneN$_3$)Br$_2$ that the crystal structure has shown. According to the Kepert method, with most rigid tridentate ligands the structure which predominates is one in which both monodentate ligands lie on the same side of the plane defined by tridentate ligand. In this orientation the metal atom is positioned above the tridentate ligand plane (defined by ABC in Figure 2a) but below the two mondentate ligands (defined by D and E in Figure 2a). The projection of the line connecting the two mondentate ligands upon the tridentate ligand plane forms a right angle to one of the triangular ABC *sides*. However, in the special case where the three donor atoms of the tridentate ligand form an equilateral triangle, as in the case here, a second structure is possible (Figure 2b). The difference between these two

structural types lies only in the position of the projection of the two monodentate ligands (D and E) upon the tridentate ligand plane. In the second case, the projection is parallel to one of the triangular ABC *sides*. This latter structure (Figure 2b) can be considered as a distorted square pyramid with the metal lying above the basal plane and approaching the fifth, apical ligand. Until now, the only monomeric compound with a structure corresponding to this second type was Cu{S[C-H$_2$CON(CH$_3$)$_2$]$_2$}Cl$_2$.[30] The two chlorine atoms in this complex are projected over the O–O edge and one S–O edge of the O–S–O triangle of donor atoms. The copper(II) complex reported here is only the second example to date of a monomeric complex exhibiting the structure represented in Figure 2b.[31]

The ⟨Cu–N⟩ and ⟨Cu–Br⟩ distances are normal for copper(II) complexes. A great deal of variation in axial ligand–copper(II) distances has been noted, and this bond is almost always longer than in-plane bonds.[32] The value here of 2.231 (42) Å for the axial ⟨Cu–N⟩ distance is moderately short and probably reflects both the highly constrained nature of the cyclic triamine and the fact that the "axial" nitrogen does not lie at a purely axial position but is distorted off the axis slightly. The electron density distribution about copper(II) has often been described as a prolate ellipsoid, and any "axial" position off the pure apical position will result in a shortened axial bond distance.[27,32]

Bond distances and angles within the cyclic triamine are quite similar to those found by Zompa and Margulis in the ([9]aneN$_3$)$_2$Ni^{2+} ion.[9] This suggests that the ligand is rather inflexible as a coordinating group, and perhaps little variation in ligand geometry of this tridentate ligand will be found.

Registry No. Cu([9]aneN$_3$)Br$_2$, 70814-02-7.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Bereman, R. D.; Giordano, R. S. *J. Am. Chem. Soc.* **1974**, *96*, 1019.
(2) Bereman, R. D.; Choi, S. N.; Wasson, J. R. *J. Inorg. Nucl. Chem.* **1975**, *87*, 2087.
(3) Bereman, R. D.; Wang, F. T.; Najdzionek, J.; Braitsch, D. M. *J. Am. Chem. Soc.* **1976**, *98*, 7266.
(4) Bereman, R. D.; Churchill, M. R.; Shields, G. *Inorg. Chem.* preceding paper in this issue.
(5) Spiro, T. S. *Acc. Chem. Res.* **1974**, *7*, 339.
(6) Gray, H. B. *Adv. Chem. Ser.* **1977**, No. 162.
(7) Zompa, L. J.; Yang, R. *Inorg. Chem.* **1976**, *15*, 1499.
(8) Zompa, L. J. *Inorg. Chem.* **1978**, *17*, 2531.
(9) Zompa, L. J.; Margulis, T. N. *Inorg. Chim. Acta* **1978**, *28*, L157.
(10) Nonoyama, M. *Transition Met. Chem.* **1976**, *1*, 70.
(11) Nonoyama, M. *Inorg. Chim. Acta.* **1976**, *20*, 53.
(12) Nonoyama, M. *J. Inorg. Nucl. Chem.* **1977**, *39*, 550.
(13) Davis, A. R.; Einstein, F. W. B.; Curtis, N. F.; Martin, J. W. L. *J. Am. Chem. Soc.* **1978**, *100*, 6258.
(14) Martin, J. W. L.; Johnston, J. H.; Curtis, N. F. *J. Chem. Soc., Dalton Trans.* **1978**, *1*, 68.
(15) Richman, J. E.; Atkins, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 2268.
(16) Koyama, H.; Yoshino, T., *Bull. Chem. Soc. Jpn.* **1972**, *45*, 481.
(17) Churchill, M. R.; Lashewycz, R.; Rotella, F. *Inorg. Chem.* **1977**, *16*, 265.
(18) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104.
(19) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.
(20) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1890.
(21) The parameter *c* is defined in the following paper: Churchill, M. R.; DeBoer, B. G.; Rotella, F. J. *Inorg. Chem.* **1976**, *15*, 1843.
(22) Wood, J. S. *Prog. Inorg. Chem.* **1972**, *16*, 227.
(23) Sacconi, L. *Transition Met. Chem.* **1968**, *4*, 220.
(24) Sacconi, L. *Pure Appl. Chem.* **1968**, *17*, 95.
(25) Phillip, A. T.; Mazurek, W.; Casey, A. T. *Aust. J. Chem.* **1971**, *24*, 501.
(26) Zeeman, J. Z. *Anorg. Allg. Chem.* **1963**, *324*, 241.
(27) Gillespie, R. J. *J. Chem. Soc.* **1963**, 4679.
(28) Burdett, J. K. *Inorg. Chem.* **1975**, *14*, 375.
(29) Kepert, D. L. *J. Chem. Soc., Dalton Trans.* **1974**, *6*, 612.
(30) Coetzee, J. A., *Acta Crystallogr., Sect. B* **1970**, *26*, 1414.
(31) The analogous copper(II) complex ([12]aneN$_3$)CuBr$_2$ has been isolated in an analytically pure but noncrystalline form in these laboratories. We would now predict a stereochemistry resembling that in Figure 2b prevails for this triamine complex on the basis of minimization of ligand repulsion energy as in the Kepert approach.
(32) Hathaway, B. J.; Billing, D. E. *Coord. Chem. Rev.* **1970**, *5*, 143.

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^{31}P NMR Studies of Catalytic Systems Containing Rhodium Complexes of Chelating Chiral and Achiral Diphosphines

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^{31}P NMR spectroscopy was utilized to determine the nature of the olefin hydrogenation catalyst species present in solution (a) on treating [RhCl(C$_2$H$_4$)$_2$]$_2$ with chelating diphosphines and (b) on treating the complexes [(NBD)Rh(diphosphine)]$^+$ with hydrogen. In all cases, reaction of the generated species with (Z)-α-acetamidocinnamic acid was also studied. A brief investigation of the oxidative addition of hydrogen, hydrogen chloride, and oxygen to bis[1,3-bis(diphenylphosphino)propane]chlororhodium(I) was carried out.

The catalytic, asymmetric reduction of prochiral olefins by rhodium(I) complexes of chiral tertiary phosphines has been an extremely active area of research in recent years.[1-3] Particularly successful catalysts have been those, modeled on the well-known, much studied Wilkinson catalyst,[4-8] RhCl(PPh$_3$)$_3$, containing chelating, bidentate diphosphine ligands. Thus complexes of rhodium(I) containing (R,R)- and (S,S)-2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane ((−)- and (+)-diop, Ia and Ib, respectively),[9] substituted derivatives of (−)-diop (II),[10] similar (R,R)- or (S,S)-trans-1,2-bis((diphenylphosphino)methyl)cycloalkanes (III–VI),[10,11] (R,R)-1,2-bis[(o-methoxyphenyl)phenylphosphino]ethane (VII),[12] (2S,3S)-bis(diphenylphosphino)-butane (S,S-chiraphos, VIII),[13] and (R)-1,2-bis(diphenylphosphino)propane (R-prophos, IX)[14] have proven to be extremely effective catalysts for the reduction of a variety of α-N-acylaminoacrylic acids to amino acid derivatives in high (60–100%) optical yields.