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A Monobridged Inner-Sphere Dimer. X-Ray Crystal Structure of μ-Cyano-bis(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)dicopper(II) Perchlorate

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The crystal and molecular structure of μ-cyano-bis(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)-dicopper(II) perchlorate, $[Cu_2(C_{16}H_{32}N_4)_2CN](ClO_4)_3$, has been determined by single-crystal X-ray diffraction methods. Crystallization occurs in the monoclinic space group *C*2/*c* with four dimers in a unit cell of dimensions $a = 24.040$ (8) Å, $b = 15.062$ (5) Å, $c = 12.525$ (4) Å, and $\beta = 98.51$ (2)°. Observed and calculated densities are 1.47 (3) and 1.50 g cm^{-3}. Solution of the structure by Patterson and Fourier techniques and least-squares refinement led to a final weighted *R* factor of 0.047 for 2941 independent reflections. The copper atom is coordinated in a distorted trigonal-bipyramidal geometry by the macrocyclic ligand and a single bridging cyanide group. Two of the perchlorate anions show O–N distances indicative of a hydrogen-bonding interaction with the macrocyclic rings.

Introduction

Linear bridged dimeric transition metal complexes can serve as model compounds for the treatment of metal-exchange interactions and also transition states for inner-sphere electron-transfer reactions. Only a few examples are known with this mode of bridging between metals of the first transition series and, of these cases, not all have been fully investigated structurally and spectroscopically. Our interest in these systems stems from previous studies on $CsCuX_3$ compounds where X = Cl or Br.[1] The bromide exists in the solid state as a polymer with linear Cu–Br–Cu bridges between $[Cu_2Br_9]^{5-}$ units and it is this interaction which is apparently the cause of the diamagnetic nature of this Cu(II) complex.

Examples of previously isolated dimeric complexes with linear cyanide bridges include $[(NC)_5FeCNCo(CN)_5]^{6-}$,[2] $(NH_3)_5CoCNCo(CN)_5$ and its linkage isomer,[3,4] $[(NC)(DMG)_2CoCNCo(DMG)_2CN]^-$ where DMG is the dimethylglyoximato ligand,[5] complexes of $[CoL_2(CN)_2]^+$ with MX_3^- species where L = 1,2-bis(diphenylphosphino)ethane and M is a variety of first-row transition metals,[6] and dimeric and trimeric organocobaloximes.[7] In the reactions of $Co(CN)_5X^{3-}$, $Co(NH_3)_5X^{2+}$, and $(H_2O)_5CrCN^{2+}$ species with $Cr(H_2O)_6^{2+}$, $Co(CN)_5^{3-}$, and other reductants, cyanide bridges have been suggested to be a structural feature of the transition state for electron transfer.[8-10]

In order better to relate magnetic, spectroscopic, and structural properties of monobridge systems, we have determined the structure of $[Cu_2([14]\text{-}4,11\text{-dieneN}_4)_2CN](ClO_4)_3$ (I) where [14]-4,11-dieneN$_4$ is 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. Compound I has previously been postulated to contain cyanide in the linear bridging mode[11] and can be compared to the related compound $[Cu_2(\text{tet } b)_2Cl](ClO_4)_3$ whose structure has been determined.[12] We recently reported the results of electronic spectral, variable-temperature magnetic, and preliminary crystallographic studies for compound I.[13]

Experimental Section

μ-Cyano-bis(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)dicopper(II) perchlorate was prepared by the method of Curtis.[11] Slow diffusion of 2-propanol into a DMSO solution of the complex produced blue single crystals up to 2 mm in length. The crystal habit was that of a thin leaf. Preliminary precession photographs (Mo Kα radiation) revealed the crystals were monoclinic with systematic absences *h*0*l*, $l = 2n + 1$, and *hkl*, $h + k = 2n + 1$, thus indicating the space group *C*2/*c* or *Cc*. A specimen for data collection was obtained by cleaving a section of dimensions 0.375 × 0.5 × 0.15 mm from a larger crystal. This was mounted on a glass fiber with the long dimension of the crystal parallel to the fiber.

Fourteen reflections were centered on a Picker four-circle diffractometer and lattice parameters obtained by least-squares refinement (*T* 23°, λ 0.71069 Å). The final values obtained were $a = 24.040$ (8) Å, $b = 15.062$ (5) Å, $c = 12.525$ (4) Å, and $\beta = 98.51$ (2)°. Flotation in a mixture of carbon tetrachloride and hexanes gave a measured density of 1.47 (3) g/cm^3, which compares well with the value 1.50 calculated assuming 4 dimers per unit cell. From ω scans, a typical peak width at half-height was found to be 0.15°, indicating an acceptable degree of mosaic spread for data collection.

Intensity data were measured on a fully automated Picker four-circle diffractometer using Mo Kα radiation monochromated by a highly oriented graphite single crystal. A θ–2θ scan technique was used with a scan width of 1.6°, a scan rate of 1°/min, and a takeoff angle of 1.6°. Stationary-background counts were measured for 10 sec before and after each peak. Three standards were measured every 60 reflections in order to monitor crystal and diffractometer stability. No systematic changes were seen. Two independent forms of data (hkl and $\bar{h}kl$; $h\bar{k}\bar{l}$ and $\bar{h}\bar{k}l$) were collected to $2\theta_{max} = 45°$ and averaged yielding 2941 independent reflections of which 2138 were considered to be observed using the criteria $I_{obsd} > 3\sigma_c(I)$. Here $\sigma_c = [T_c + 0.25(t_c/t_b)^2(B_1 + B_2)]^{1/2}$ where T_c is the total counts, t_c/t_b is the ratio of the time counting peak intensity to that spent counting backgrounds, and B_1 and B_2 are the background counts. Lorentz-polarization corrections and calculation of the observed structure factor amplitudes from the raw data were carried out using the local program GORDO. An absorption correction was applied with the program ORABS[14] ($\mu = 12.3$ cm^{-1}) giving a range of transmission coefficients from 0.675 to 0.869. During the structure solution and early refinement, a data set was used consisting only of observed

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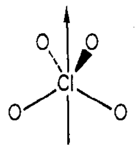
reflections from one form. Final refinement using the averaged data set (2941 reflections) was carried out with weights assigned on the basis of counting statistics. No significant systematic variation of $w(F_o - F_c)^2$ was seen with respect to $(\sin \theta)/\lambda$ or the magnitude of the structure factors. The C, N, Cl, O, and Cu scattering factors were taken from the tabulation of Cromer and Waber[15] and the hydrogen scattering factors from Stewart, *et al.*[16] Anomalous dispersion corrections used for the copper and chlorine atoms were those of Cromer and Liberman.[17]

Solution and Refinement of Structure

The structure was solved by standard heavy-atom methods. A Patterson map revealed the copper atom position and subsequent Fourier calculations[18] in the centrosymmetric space group resulted in the location of all nonhydrogen atoms except the oxygen atoms of the perchlorate anion situated at 0, y, $^1/_2$, which appeared to be disordered. In the centrosymmetric space group, only half the dimer is unique, the cyanide group being situated on a center of inversion. Since the carbon and nitrogen ends of the cyanide group are indistinguishable, an average of the C and N scattering factors was used for these two atoms. With isotropic thermal parameters and no disorder model for the above perchlorate, least-squares refinement gave convergence at an $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ of 0.124. The noncentrosymmetric space group was initially ruled out on the basis of an $N(Z)$ test[19] which showed the distribution of intensities closely matched the theoretical centrosymmetric distribution. An attempted isotropic refinement in the *Cc* space group led to chemically unreasonable bond distances. In addition, at isotropic convergence in the noncentrosymmetric space group, a difference Fourier with no cyanide group input still showed both cyanide atoms to have the same integrated electron density. All subsequent refinement was therefore carried out in the centrosymmetric space group.

At this point, an absorption correction was applied and the two forms of data were averaged. The nondisordered perchlorate anion had very large thermal parameters and, in an effort to fit the large librations, the third cumulant of the probability density function was included during latter stages of refinement for these oxygen atoms.[20] Insertion of hydrogen atoms at their calculated positions using a bond length of 0.95 Å and the appropriate carbon hybridization followed by further refinement of the nonhydrogen atoms with anisotropic thermal parameters gave an $R_2 = (\Sigma w(F_o - F_c)^2/\Sigma w \cdot F_o^2)^{1/2}$ of 0.094. A difference Fourier indicated that the best model to fit the disordered perchlorate was that of a superposition of equivalent amounts of orientations A and B on a crystallographic twofold axis. Form B is further disordered due to the twofold axis passing through the chlorine and one oxygen. Although the hydrogen atom positions were not varied, the rotational orientation of the methyl groups was set to correspond to that observed on a difference Fourier map. Convergence so that the maximum shift in all parameters was less than one-tenth the estimated standard deviation (except for disordered oxygen atoms) led to the final R factors: $R_2 = 0.047$, $R_1 = 0.071$. A final difference Fourier map had no peaks higher than 0.28 e/Å^3 and the estimated standard deviation of an observation of unit weight was 1.35. Tables I-III list the positional and thermal parameters obtained; see paragraph at end of paper regarding supplementary material.



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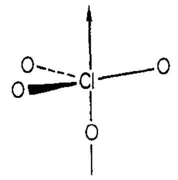

B

Table I. Positional Parameters for Nonhydrogen Atoms in $\{[Cu(C_{16}H_{32}N_4)]_2(CN)\}(ClO_4)_3$

Atom	x	y	z
Cu	0.15844 (2)[b]	0.20302 (3)	0.08809 (4)
Cl(1)	0.0000	0.1412 (2)	0.2500
Cl(2)	0.1376 (1)	0.2966 (1)	−0.3414 (2)
N(1)	0.2048 (2)	0.1341 (3)	0.2125 (3)
N(2)	0.1191 (2)	0.0923 (2)	0.0215 (3)
N(3)	0.1047 (2)	0.2665 (2)	−0.0308 (3)
N(4)	0.1443 (2)	0.2886 (2)	0.2051 (3)
C(1)	0.2049 (2)	0.0344 (3)	0.2026 (4)
C(2)	0.2320 (2)	−0.0077 (4)	0.3092 (4)
C(3)	0.2405 (2)	0.0118 (4)	0.1176 (4)
C(4)	0.1458 (2)	−0.0012 (3)	0.1766 (4)
C(5)	0.1143 (2)	0.0187 (3)	0.0666 (4)
C(6)	0.0764 (2)	−0.0540 (4)	0.0208 (5)
C(7)	0.0872 (2)	0.1154 (3)	−0.0821 (4)
C(8)	0.0606 (2)	0.2050 (3)	−0.0722 (4)
C(9)	0.0856 (2)	0.3589 (3)	−0.0040 (4)
C(10)	0.0399 (2)	0.3916 (3)	−0.0915 (5)
C(11)	0.1368 (2)	0.4190 (3)	−0.0010 (4)
C(12)	0.0638 (2)	0.3592 (3)	0.1023 (4)
C(13)	0.1049 (2)	0.3435 (3)	0.2045 (4)
C(14)	0.0928 (2)	0.3965 (4)	0.2985 (5)
C(15)	0.1825 (2)	0.2676 (4)	0.3036 (4)
C(16)	0.1889 (2)	0.1697 (4)	0.3118 (4)
Cyanide[a]	0.2306 (1)	0.2393 (3)	0.0185 (3)
O(1)	0.1713 (5)	0.2687 (13)	−0.4042 (11)
O(2)	0.0918 (5)	0.2530 (8)	−0.3335 (10)
O(3)	0.1664 (5)	0.2991 (14)	−0.2545 (10)
O(4)	0.1250 (8)	0.3676 (12)	−0.3721 (20)
O(5)	0.0304 (10)	0.1986 (11)	0.3319 (18)
O(6)	0.0318 (7)	0.0881 (17)	0.2048 (18)
O(7)	0.0000	0.0490 (12)	0.2500
O(8)	0.0268 (17)	0.1491 (20)	0.1609 (25)
O(9)	0.0518 (9)	0.1683 (24)	0.2566 (40)
O(10)	0.0434 (44)	0.1592 (44)	0.3162 (72)

[a] Since the cyanide group is disordered about a center of inversion only one average position is given for the C and N. [b] Numbers in parentheses in all tables are estimated standard deviations of the least significant digits.

Discussion

The geometry about the copper atom is essentially that of a trigonal bipyramid with the inflexibility of the ligand causing some distortion, principally in opening the N(2)-Cu-N(4) angle to 134.6 (1)°. Other deviations from ideal trigonal-bipyramidal geometry include a bending of both the Cu-N(1) and Cu-N(3) bonds back from the bridge, the N(1)-Cu-cyanide and N(3)-Cu-cyanide angles being 93.3 (1) and 92.7 (1)°, respectively. Calculation of the angle between the planes defined by N(1), X, N(3) and N(2), X, N(4) shows that the trigonal plane is tilted by 5.5° from an orientation perpendicular to that containing the axial nitrogen atoms and the cyanide bridge. A slight increase is observed in the two axial Cu-N bond lengths (2.056 (3) Å average) compared to the average value of 2.026 (3) Å in the trigonal plane as shown in Figure 1. The CN^- bridge is nearly linear with a Cu-C-N (and Cu-N-C) angle of 178.6 (5)°.

Bond distances and angles in the macrocyclic ligand are similar to those found in previous crystallographic stud-

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(18) A set of computer programs from Picker Nuclear, Inc., was utilized for automatic operation of the diffractometer. The general plane Fourier mapping program, JIMDAP, modified by J. Ibers and F. Ross from the original version FORDAP by H. Zalkin and D. H. Templeton, was used to calculate Fourier maps. Least-squares programs used were a local version of ORFLS by W. R. Busing, K. O. Martin, and H. A. Levy and ORXFLS3 based on ORFLS with modifications by R. D. Ellison, W. C. Hamilton, J. A. Ibers, C. K. Johnson, and W. E. Thiessen. Standard deviations were calculated using ORFFE3 modified by G. M. Brown, C. K. Johnson, and W. E. Thiessen from ORFFE by W. R. Busing, K. O. Martin, and H. A. Levy. ORTEP by C. K. Johnson was used to plot the molecular structures and theoretical hydrogen atom positions were calculated from known atomic positions and hybridizations using HYGEN by F. K. Ross.

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Table II. Anisotropic Thermal Parameters for Nonhydrogen Atoms[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.00160 (1)	0.00365 (3)	0.00574 (4)	0.00005 (2)	0.00027 (2)	0.00021 (3)
Cl(1)	0.00199 (4)	0.00757 (15)	0.00855 (17)	0.00000	0.00120 (7)	0.00000
Cl(2)	0.00257 (4)	0.00782 (10)	0.00969 (13)	−0.00049 (6)	0.00008 (6)	0.00042 (11)
N(1)	0.00196 (8)	0.00592 (25)	0.00694 (33)	0.00018 (12)	0.00073 (13)	0.00059 (23)
N(2)	0.00202 (9)	0.00396 (21)	0.00721 (31)	0.00010 (11)	0.00067 (13)	0.00070 (22)
N(3)	0.00166 (8)	0.00543 (23)	0.00721 (30)	0.00019 (11)	0.00068 (12)	0.00046 (21)
N(4)	0.00212 (8)	0.00526 (23)	0.00837 (33)	−0.00012 (12)	0.00123 (14)	−0.00039 (24)
C(1)	0.00236 (11)	0.00461 (28)	0.00696 (39)	0.00073 (15)	0.00080 (17)	0.00192 (26)
C(2)	0.00406 (17)	0.00771 (38)	0.01120 (55)	0.00033 (21)	−0.00017 (25)	0.00288 (38)
C(3)	0.00253 (13)	0.00705 (34)	0.01170 (51)	0.00107 (17)	0.00131 (21)	0.00198 (35)
C(4)	0.00254 (12)	0.00449 (27)	0.00924 (44)	−0.00010 (15)	0.00087 (19)	0.00111 (28)
C(5)	0.00177 (10)	0.00432 (28)	0.00848 (42)	−0.00018 (14)	0.00096 (17)	−0.00056 (29)
C(6)	0.00393 (17)	0.00530 (34)	0.01619 (68)	−0.00070 (20)	−0.00091 (27)	0.00176 (39)
C(7)	0.00265 (12)	0.00480 (30)	0.00768 (41)	−0.00024 (16)	0.00018 (18)	−0.00054 (29)
C(8)	0.00193 (10)	0.00559 (29)	0.00841 (39)	−0.00059 (16)	−0.00001 (16)	0.00035 (31)
C(9)	0.00169 (10)	0.00382 (26)	0.01101 (46)	0.00084 (13)	0.00091 (17)	0.00097 (28)
C(10)	0.00236 (12)	0.00561 (32)	0.01531 (60)	0.00096 (17)	0.00049 (22)	0.00156 (37)
C(11)	0.00270 (13)	0.00475 (29)	0.01224 (51)	−0.00014 (16)	0.00110 (20)	0.00119 (32)
C(12)	0.00257 (13)	0.00509 (31)	0.01296 (58)	0.00088 (16)	0.00236 (22)	−0.00020 (33)
C(13)	0.00254 (12)	0.00489 (29)	0.00965 (48)	−0.00022 (15)	0.00228 (20)	−0.00104 (30)
C(14)	0.00387 (18)	0.01027 (47)	0.01487 (66)	0.00064 (24)	0.00225 (27)	−0.00477 (48)
C(15)	0.00291 (14)	0.00781 (40)	0.00657 (43)	−0.00058 (18)	0.00036 (20)	−0.00088 (32)
C(16)	0.00299 (14)	0.00731 (37)	0.00696 (45)	0.00005 (18)	0.00072 (20)	0.00019 (31)
Cyanide[b]	0.00148 (9)	0.00470 (23)	0.00638 (34)	0.00041 (13)	0.00068 (13)	0.00132 (22)
O(1)	0.00541 (18)	0.03983 (113)	0.02170 (73)	−0.00065 (37)	0.00546 (33)	−0.01213 (79)
O(2)	0.00406 (14)	0.01197 (37)	0.03321 (87)	−0.00166 (21)	0.00233 (28)	−0.00549 (49)
O(3)	0.00420 (15)	0.03926 (113)	0.01388 (55)	−0.00357 (33)	−0.00030 (24)	−0.00173 (63)
O(4)	0.00964 (34)	0.01735 (68)	0.06608 (216)	0.00129 (41)	0.00559 (72)	0.02387 (107)
O(5)	0.00433 (46)	0.00724 (72)	0.01309 (142)	−0.00078 (44)	−0.00024 (56)	−0.00435 (86)
O(6)	0.00356 (79)	0.03240 (286)	0.02465 (348)	0.00640 (135)	0.00237 (104)	−0.01189 (332)
O(7)	0.00245 (60)	0.00710 (94)	0.02308 (317)	0.00000	0.00203 (81)	0.00000
O(8)	0.00449 (94)	0.01217 (203)	0.00884 (189)	−0.00526 (130)	0.00470 (115)	−0.00231 (148)
O(9)	0.00094 (41)	0.01046 (182)	0.02670 (606)	−0.00275 (69)	0.00032 (125)	0.00760 (281)
O(10)	0.00972 (264)	0.01998 (598)	0.02479 (735)	0.00020 (270)	−0.01006 (332)	0.00451 (522)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Average of C and N for disordered cyanide group.

Table III. Third Cumulant Elements for Perchlorate Oxygen Atoms[a]

Atom	C_{111}	C_{222}	C_{333}	C_{112}	C_{122}	C_{113}	C_{133}	C C_{223}	C_{233}	C_{123}
O(1)	−6 (2)	370 (33)	165 (18)	11 (3)	14 (8)	−7 (3)	39 (6)	−50 (17)	−78 (13)	−1 (5)
O(2)	6 (2)	35 (8)	−82 (24)	−8 (2)	0.4 (3)	13 (2)	39 (6)	−26 (6)	53 (10)	−9 (3)
O(3)	−7 (2)	−20 (32)	−37 (12)	5 (3)	−37 (7)	−8 (2)	11 (4)	−173 (12)	0.5 (10)	17 (4)
O(4)	39 (5)	−84 (15)	157 (72)	−16 (4)	−36 (6)	−5 (7)	17 (18)	−190 (18)	−208 (30)	−27 (8)

[a] Elements multiplied by 10^5.

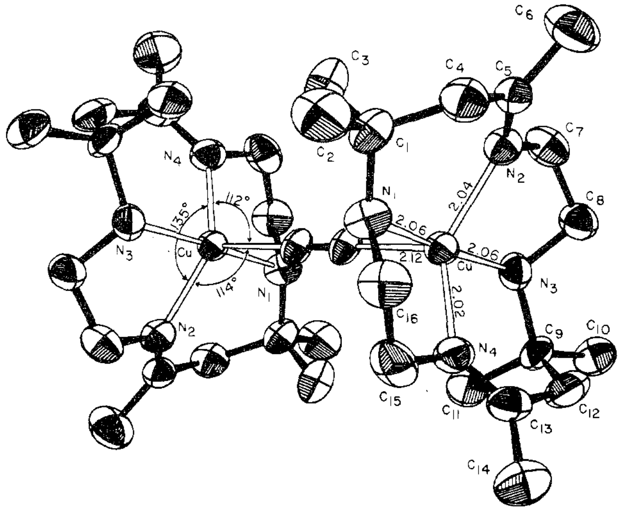

Figure 1. Molecular structure of the dimeric cation in $[Cu_2([14]\text{-}4,11\text{-dieneN}_4)_2CN](ClO_4)_3$. Thermal ellipsoids are shown at the 40% probability level and perchlorate anions omitted for clarity.

ies.[21-23] (See Tables IV and V.) In particular, the largest deviation of bond angles from that expected considering the hybridization occurs for the C(1)-C(4)-C(5) angle of 117.2 (4)° and the C(9)-C(12)-C(13) angle of 118.6 (4)°. This concentration of strain in the six-membered rings has also been observed in Ni(II)[24] and Co(III)[25] complexes containing macrocycles with cis imine bonds. Bailey and Maxwell[23] have suggested this distortion around the methylene carbon of the six-membered ring may be due to interactions of the methyl groups. The N(2)-C(5) and N(4)-C(13) bond lengths fall just below the usual range of 1.26-1.29 Å found for unconjugated imine bonds. However, the difference is only about one standard deviation of the bond length so this is not a significant contraction. One might expect that some anomalous bond lengths would be observed as a result of the large amount of disorder in the perchlorate anions, but the only scatter in chemically equivalent bonds which is even on the borderline of being significant is between C(1)-

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Table IV. Interatomic Distances (A) for Nonhydrogen Atoms[a]

Atoms	Distance	Atoms	Distance
Cu-N(1)	2.057 (4)	C(9)-C(11)	1.523 (6)
Cu-N(2)	2.035 (4)	C(9)-C(12)	1.502 (6)
Cu-N(3)	2.056 (4)	C(12)-C(13)	1.516 (7)
Cu-N(4)	2.018 (4)	C(13)-C(14)	1.487 (7)
Cu-cyanide[b]	2.125 (3)	C(13)-N(4)	1.255 (6)
N(1)-C(1)	1.506 (6)	N(4)-C(15)	1.460 (6)
N(1)-C(16)	1.457 (6)	C(15)-C(16)	1.484 (7)
C(1)-C(2)	1.534 (6)	Cl(1)-O(5)	1.454 (17)
C(1)-C(3)	1.500 (6)	Cl(1)-O(6)	1.294 (14)
C(1)-C(4)	1.509 (6)	Cl(1)-O(7)	1.388 (17)
C(4)-C(5)	1.501 (6)	Cl(1)-O(8)	1.374 (21)
C(5)-C(6)	1.485 (6)	Cl(1)-O(9)	1.302 (18)
C(5)-N(2)	1.257 (5)	Cl(1)-O(10)	1.261 (62)
N(2)-C(7)	1.449 (5)	Cl(2)-O(1)	1.280 (12)
C(7)-C(8)	1.505 (6)	Cl(2)-O(2)	1.298 (11)
C(8)-N(3)	1.445 (5)	Cl(2)-O(3)	1.201 (11)
N(3)-C(9)	1.520 (5)	Cl(2)-O(4)	1.161 (14)
C(9)-C(10)	1.514 (6)	Cyanide[b]	1.147 (6)

[a] Error in lattice parameters included in estimated standard deviations. [b] Cyanide atom position taken as that of an atom with scattering factors the average of carbon and nitrogen due to disorder about a center of inversion.

Table V. Bond Angles (deg) for Nonhydrogen Atoms

Atoms	Angle	Atoms	Angle
	Cu Coordination Angles		
N(1)-Cu-N(2)	93.6 (2)	N(3)-Cu-N(4)	94.2 (2)
N(1)-Cu-N(3)	174.0 (1)	N(1)-Cu-cyanide[a]	93.3 (1)
N(1)-Cu-N(4)	84.4 (2)	N(2)-Cu-cyanide	113.7 (2)
N(2)-Cu-N(3)	83.1 (1)	N(3)-Cu-cyanide	92.7 (1)
N(2)-Cu-N(4)	134.6 (1)	N(4)-Cu-cyanide	111.7 (2)
	Ligand Angles		
N(1)-C(1)-C(2)	110.3 (4)	N(3)-C(9)-C(10)	110.4 (4)
C(4)-C(1)-C(2)	107.7 (4)	C(12)-C(9)-C(10)	109.3 (4)
N(1)-C(1)-C(3)	107.1 (4)	N(3)-C(9)-C(11)	106.2 (3)
C(4)-C(1)-C(3)	112.6 (4)	C(12)-C(9)-C(11)	111.2 (4)
N(1)-C(1)-C(4)	111.0 (4)	N(3)-C(9)-C(12)	110.8 (4)
C(2)-C(1)-C(3)	108.1 (4)	C(11)-C(9)-C(10)	108.8 (4)
C(1)-C(4)-C(5)	117.2 (4)	C(9)-C(12)-C(13)	118.6 (4)
C(4)-C(5)-N(2)	121.5 (4)	C(12)-C(13)-C(14)	113.9 (4)
C(4)-C(5)-C(6)	113.8 (4)	C(12)-C(13)-N(4)	120.3 (4)
N(2)-C(5)-C(6)	124.6 (4)	C(14)-C(13)-N(4)	125.8 (5)
C(5)-N(2)-C(7)	122.9 (4)	C(13)-N(4)-C(15)	121.8 (4)
N(2)-C(7)-C(8)	108.4 (4)	N(4)-C(15)-C(16)	108.7 (4)
C(7)-C(8)-N(3)	107.9 (4)	C(15)-C(16)-N(1)	110.1 (4)
C(8)-N(3)-C(9)	115.9 (3)	C(16)-N(1)-C(1)	116.2 (4)
	Perchlorate Angles		
O(1)-Cl(2)-O(2)	120 (1)	O(8)-Cl(1)-O(9′)	119 (2)
O(1)-Cl(2)-O(3)	104 (1)	O(8)-Cl(1)-O(10)	94 (5)
O(1)-Cl(2)-O(4)	105 (1)	O(9′)-Cl(1)-O(10)	132 (5)
O(2)-Cl(2)-O(3)	109 (1)	O(5)-Cl(1)-O(6)	114 (1)
O(2)-Cl(2)-O(4)	108 (1)	O(5)-Cl(1)-O(6′)	109 (2)
O(3)-Cl(2)-O(4)	111 (1)	O(5)-Cl(1)-O(5′)	107 (2)
O(7)-Cl(1)-O(8)	95 (1)	O(6)-Cl(1)-O(6′)	104 (3)
O(7)-Cl(1)-O(9′)[b]	108 (2)	O(6)-Cl(1)-O(5′)	109 (2)
O(7)-Cl(1)-O(10)	102 (3)	O(6′)-Cl(1)-O(5′)	114 (1)

[a] See footnote *b*, Table IV. [b] Primed numbers represent atomic positions generated by the twofold axis at 0, *y*, 1/4.

C(3) and C(9)-C(11) and between C(1)-C(2) and C(9)-C(10).

Two of the perchlorate anions are situated so that O(3) is positioned between the macrocycles on either end of the dimer and help to stabilize the structure by hydrogen bonding to the saturated nitrogen atoms. The distances found for this interaction were 3.225 (11) Å for O(3) to N(1′) (see footnote *a*, Table VI) and 3.394 (11) Å for O(3) to N(3). Since these two perchlorates show very large thermal parameters for all oxygen atoms, the O-Cl distance increasing over 0.1 Å when corrected for thermal motion using a riding model (Table VI), these hydrogen-bonding distances calculated from uncorrected oxygen atom positions probably represent upper limits. This was the only significant interaction by this perchlorate, all other distances of approach being greater than 3.5 Å.

Table VI. Bond Lengths and Hydrogen-Bonding Distances for Bridging $\mathrm{ClO_4^-}$ (Å)

Atoms	Distance	Distance corrected for thermal motion (riding model)
Cl(2)-O(1)	1.280 (12)	1.487 (12)
Cl(2)-O(2)	1.298 (11)	1.389 (11)
Cl(2)-O(3)	1.201 (11)	1.375 (12)
Cl(2)-O(4)	1.161 (14)	1.472 (14)
O(3)-N(1′)[a]	3.225 (11)	
O(3)-N(3)	3.394 (11)	

[a] Primed number represents an atomic position generated by the center of inversion at 1/4, 1/4, 0.

It was felt that the large thermal motion of the perchlorate oxygen atoms would be poorly fit by a normal anisotropic temperature factor and so a model including the third cumulant of the probability density function was used for O(1) through O(4). This resulted in a significantly improved fit to the data as shown by employment of Hamilton's *R* factor ratio test on the 99.5% confidence level.[26] The nondisordered perchlorate has an average Cl-O bond length of 1.43 Å after correction for thermal motion and an average O-Cl-O angle of 109.5°. Accepted values for perchlorate bond lengths are in the range 1.44-1.46 Å.[27,28] Static disorder was found for the second unique perchlorate which is situated on the special position 0, *y*, 1/4. A satisfactory fit to the data was obtained by assuming an equal distribution between an orientation with the crystallographic twofold axis along the twofold axis of the tetrahedron and one with the tetrahedral threefold axis along the crystallographic twofold axis. This second orientation also necessarily has disordered oxygen atoms off the twofold axis. Due to the large amount of disorder, no third cumulant elements were included for any of these atoms.

Disordering of the bridging cyanide group about a center of inversion prevented identification of the carbon and nitrogen atoms. The thermal parameters of the atoms used for cyanide (scattering factors taken as the average of carbon and nitrogen values) are not large compared to those of the other carbon and nitrogen atoms in the structure (Table II). Even comparison of the root-mean-square displacement of the atom representing the cyanide in the direction of the Cu-Cu vector with that perpendicular to this direction did not show any clear disorder. It is interesting to note that in the structure of $\mathrm{[Cu(diene)CN]ClO_4}$[29] which contains a cyanide group bridging Cu(II) atoms, the Cu-C and Cu-N bond lengths are 1.995 (4) and 2.348 (4) Å, respectively, giving 2.172 Å as an average. In compound I, the copper-cyanide distance is 2.125 (3) Å, although it must be pointed out that the geometry in $\mathrm{[Cu(diene)CN]ClO_4}$ is a distorted square pyramid and the bridging is from an axial to an equatorial position of another complex while in I the bridge is between two equatorial positions of the trigonal bipyramids. The value of 1.147 (6) Å for the cyanide bond length is within the 1.145-1.163 Å range

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(26) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).
(27) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p 321, Table 9-2.
(28) D. W. J. Cruikshank, *J. Chem. Soc.*, 5486 (1961).
(29) S. C. Yang and P. W. R. Corfield, to be submitted for publication.

found in CN$^-$-bridged Cu(I)–Cu(II) systems[30] and the 1.096–1.152 Å variation in some Cu(I) polymeric compounds.[31] As has been discussed elsewhere,[11,13] the ir spectrum of I shows a weak cyanide stretch at 2130 cm^{-1} which is shifted to higher frequency compared to a terminal cyanide in five-coordinate Cu(II) complexes, a well-known property of bridging cyanide groups. Scarcity of structural data on Cu(II) cyanide-bridged systems prevents comparison with more closely related species.

It has been found[13] from a variable-temperature magnetic study (4.2–283°K) that the copper atoms in compound I are antiferromagnetically coupled through the cyanide bridge ($J = -4.8$ cm^{-1}). This must be an intradimer interaction since the structure consists of isolated dimer units arranged in chains with intervening perchlorate anions. There are two dimer orientations present which are related by a crystallographic twofold axis, but within each dimer the coordination spheres of the copper atoms are aligned due to positioning about a center of inversion. Room-temperature Q-band powder esr spectra of I show three **g** values which could arise from a slight misalignment of the **g** tensors on the two ends of the dimer due to one copper atom having a cyanide carbon atom bonded to it and the other a cyanide nitrogen.[13] Structurally, this misalignment is not observed. Differentiation of this explanation from others such as rhombic symmetry will require comprehensive esr single-crystal or spectral simulation studies.

The structure of $[Cu_2(\text{tet } b)_2Cl](ClO_4)_3$, where tet *b* is a saturated analog of the macrocycle in I, has been recently determined[12] and, while it does not contain cyanide, general similarities of this compound to I can be noted. It is observed that the chloride forms a nearly linear bridge between the two copper atoms but the metal–metal distance is somewhat shorter (5.0 Å instead of the 5.4 Å found in the cyanide dimer) and the exchange interaction is larger ($J = -144$ cm^{-1}). Although these two complexes crystallize in the same space group, the chloride bridge is situated on a twofold axis rather than an inversion center and this results in the coordination spheres of the two copper atoms in each dimer being skewed with respect to each other. The greater length of the cyanide compared to the chloride bridge is certainly one factor which is important in reducing the exchange, and changes in the orientation of the axes of the g tensors with respect to the bridge direction caused by differing amounts of distortion from trigonal-bipyramidal geometry and differing strengths of the Cu–bridge bonds in the two cases are also likely to have an important effect.

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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 \$2.00 for microfiche, referring to code number INORG-74-2404.

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Crystal and Molecular Structure of η^5-Cyclopentadienyl(triphenylphosphine)carbonyliridium, $(\eta^5\text{-}C_5H_5)IrP(C_6H_5)_3(CO)$

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The crystal and molecular structure of η^5-cyclopentadienyl(triphenylphosphine)carbonyliridium, $(\eta^5\text{-}C_5H_5)IrP(C_6H_5)_3(CO)$, has been determined from three-dimensional single-crystal X-ray data collected by counter methods. This compound crystallizes as discrete molecules in the triclinic space group $P\bar{1}$ with two molecules per reduced cell of dimensions $a = 10.028$ (4) Å, $b = 10.578$ (4) Å, $c = 11.291$ (4) Å, $\alpha = 72.06$ (4)°, $\beta = 81.56$ (4)°, and $\gamma = 62.53$ (4)°. The structure has been refined by full-matrix least-squares methods to a conventional R factor of 0.033 for the 2525 significant intensities. The cyclopentadienyl ring center, triphenylphosphine, and carbonyl groups form a planar, triangular array with the central iridium atom. The iridium–phosphorus distance is 2.237 (2) Å, and the average iridium–carbon(cyclopentadienyl) distance is 2.272 (5) Å.

Introduction

Oxidative addition reactions, of d^8 complexes in particular, have been the subject of much interest.[1,2] One interesting class of d^8 complexes comprises compounds of the type $(C_5H_5)MLL'$, where M = Co, Rh, or Ir and L and L$'$ may be a combination of tertiary phosphines, carbonyls, and olefins. Until lately work was directed mainly at the cobalt and rhodium members of this group. Recently Oliver and Graham[3] reported a facile synthesis and some interesting reactions of the iridium compound $(C_5H_5)IrP(C_6H_5)_3(CO)$, **1**, and this has been followed by a kinetic study.[4] These studies showed that **1** exhibits substantial nucleophilic character in reactions

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