Contribution from the Department of Chemistry,
University of Kansas, Lawrence, Kansas 66045

Crystal and Molecular Structure of a Silver(II) Complex with a Synthetic Macrocyclic Ligand

KRISTIN BOWMAN MERTES

Received August 22, 1977

The crystal and molecular structure of *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecanesilver(II) nitrate was performed by three-dimensional x-ray crystallographic techniques. The complex crystallizes in the monoclinic space group (C_{2h}^6) $C2/c$ with cell dimensions a = 13.222 (3) Å, b = 11.629 (4) Å, c = 15.471 (3) Å, β = 111.87 (2)°, and Z = 4. The structure was solved by Fourier and least-squares techniques to a conventional R = 0.033 for 2268 reflections with $I \geq 3\sigma(I)$. The silver sits on a crystallographic inversion center and is surrounded by a square-planar array of nitrogen atoms at an average distance of 2.160 (3) Å. Axial interactions with nitrate oxygens result in distorted octahedral coordination in which Ag–O is 2.807 (4) Å.

Introduction

Studies of transition-metal complexes with synthetic macrocyclic ligands have been of great interest in recent years not only because of the possibilities for mimicking certain biological systems but also for the usefulness of these compounds in elucidating structure–reactivity relationships, i.e., the steric and electronic influences of the ligand on the reactivity of the metal ion. One dominant characteristic of the synthetic macrocyclic ligands is the stability which they impart to the resulting complexes, an example of which is the increased occurrence in these compounds of metal ions in unusual oxidation states. While numerous studies in this area of the first transition series have appeared,[1] reports of investigations with other transition metals are limited.

One example of stabilization of unusual oxidation states with macrocyclic ligands is found with silver(II). The propensity of divalent silver to act as an oxidizing agent is well documented.[2] As a result, until relatively recently silver(II) complexes were rare and were stable only when formed with ligands which could survive the strong oxidizing capabilities of silver(II). For the most part these ligands have been nitrogen-containing unsaturated heterocycles such as pyridines, polypyridines, and related compounds.[3,4] In 1972, Kestner and Allred reported that when $AgClO_4$ or $AgNO_3$ was added to a methanolic solution of 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane ([14]ane, a completely saturated synthetic macrocyclic ligand) disproportionation of the silver(I) to elemental silver and a silver(II) complex with the ligand occurred.[5] The following year Barefield and Mocella found that a variety of these macrocyclic complexes could be made and described the synthesis and physical properties of a series of these in which the nature of the peripheral substituents and ligand saturation were varied.[6]

The structural determination of the nitrate salt of one of these complexes, [Ag(*meso*-[14]ane)][NO_3]$_2$, was undertaken for three basic reasons. First, there is a general paucity of structural data for silver(II) complexes. Second, the structural characteristics of synthetic macrocyclic compounds are interesting because of applications in biological areas as well as the aptitude of macrocyclic ligands for controlling the reactivity of the metal ion with which they are complexed. Third, and of major importance, is the somewhat unique aspect of the fully saturated macrocyclic ligand in the realm of silver(II) complexes.

Experimental Section

Crystals suitable for structural determination were obtained by slow crystallization of [Ag(*meso*-[14]ane)][NO_3]$_2$ from water in the absence of light. Preliminary precession photographs indicated the complex crystallizes in the monoclinic space group Cc or $C2/c$ according to the observed conditions for reflection hkl, $h + k = 2n$.

A small crystal (0.25 × 0.20 × 0.30 mm) was chosen and mounted in a random orientation on a Syntex $P2_1$ automatic diffractometer equipped with a scintillation counter and graphite monochromator. Accurate centering of 15 reflections well distributed in reciprocal space, of which 11 had $2\theta > 10°$, resulted in unit cell dimensions a = 13.222 (3) Å, b = 11.629 (4) Å, c = 15.471 (3) Å, β = 111.87 (2)°, and V = 2207.4 (9) Å^3.[7] The measured density of 1.55 (1) g cm^{-3} obtained by flotation in CCl_4–hexane agrees with the calculated density of 1.55 g cm^{-3} for $Z = 4$.

The data were collected on a fully automated Syntex $P2_1$ diffractometer equipped with a pulse height analyzer, a scintillation counter, and a graphite monochromator. Mo Kα radiation was used with a takeoff angle of 6.2°. The θ–2θ scan technique was employed with a variable scan rate ranging from 1.0 to 29.3°/min to collect data to $2\theta \leq 60°$. The scan range ran from 1° below the Kα_1 peak to 1° above Kα_2 with background counts taken with a background to scan ratio of 1.0 at the beginning and end of each 2θ scan. Three standard reflections ($5,\bar{1},5$; $2,0,\bar{4}$; and $3,1,\bar{5}$) were measured every 97 reflections. A total of 3248 independent reflections were collected of which 2268 had $I \geq 3\sigma(I)$ and were used in data analysis. Intensities and standard deviations were calculated according to the formulas $I = r(S - RB)$ and $\sigma_I^2 = r^2(S + R^2B)$, respectively, where r is the scan rate in degrees per minute, S is the total scan count, R is the scan to background time ratio, and B is the total background count. For intensities falling in the ranges from 5000 to 50000 Hz, coincidence corrections were made according to $I_t = I_0 + \tau I_0^2$.[8] This is an approximation to the actual Schiff formula for calculation of true intensity values,[9] $I_t = I_0 e^{I_t \tau}$ where I_t is the corrected count, I_0 the observed uncorrected count, and τ is the counter circuit dead time.

The data were corrected for background, and Lorentz and polarization factors were applied to obtain the structure factors. Because of the small linear absorption coefficient of 9.36 cm^{-1} and the small size of the crystal, no absorption corrections were made. Wilson's method was used to bring the F^2 to a relatively absolute scale. The decrease in intensity of the three standard reflections was 3.5%. The data were scaled accordingly, after which the root mean square deviation of the standards became 1.9%. At this point σ_I^2 was also scaled by increasing the σ_I^2 obtained by counting statistics by $p\sigma_I^2$ where p was chosen as the root-mean-square deviation of the standard reflections, 0.019, according to Corfield et al.[10]

The structure was solved by the heavy-atom method[11] and refined by full-matrix least-squares techniques during which the function $\sum w(|F_o| - |F_c|)^2$ was minimized. Weights used were $1/\sigma_F^2 = 4LpI/\sigma_I^2$.

Structure Determination and Refinement

Examination of the hkl reflections revealed that all $k + l \neq 2n$ were weak or absent. This observation, along with the four required molecules per unit cell, and examination of the Patterson map suggested that the silver was located at the special position $^1/_4$, $^1/_4$, $^1/_2$ in the space group $C2/c$. Successful refinement of the structure confirmed the choice of space groups. The remainder of the nonhydrogens were located from the subsequent Fourier. Scattering factor tables for Ag were obtained from Cromer and Waber,[12] for C, N, and O from Cromer and Mann,[13] and from Ibers for H and anomalous factors for Ag.[14]

0020-1669/78/1317-0049$01.00/0

Table I. Final Positional and Thermal Parameters for Nonhydrogen Atoms in [Ag(*meso*-[14]ane)][NO_3]$_2$[a]

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ag	0.2500	0.2500	0.5000	0.00418 (2)	0.00482 (2)	0.00316 (2)	−0.00032 (2)	0.00164 (1)	0.00017 (2)
N(1)	0.1863 (2)	0.0767 (2)	0.4834 (2)	0.0041 (2)	0.0046 (2)	0.0037 (1)	−0.0003 (1)	0.0014 (1)	0.0000 (1)
C(1)	0.2386 (3)	−0.0116 (3)	0.4443 (2)	0.0047 (2)	0.0046 (2)	0.0044 (2)	−0.0003 (2)	0.0015 (2)	−0.0002 (2)
C(1A)	0.1619 (4)	−0.1162 (3)	0.4121 (4)	0.0088 (4)	0.0058 (3)	0.0085 (3)	−0.0021 (3)	0.0034 (3)	−0.0023 (2)
C(1B)	0.3474 (3)	−0.0496 (3)	0.5174 (3)	0.0064 (3)	0.0068 (3)	0.0057 (2)	0.0022 (2)	0.0019 (2)	0.0016 (2)
C(2)	0.2544 (3)	0.0383 (3)	0.3577 (2)	0.0054 (2)	0.0064 (2)	0.0036 (2)	0.0002 (2)	0.0012 (2)	−0.0010 (2)
C(3)	0.3397 (3)	0.1316 (3)	0.3701 (2)	0.0047 (2)	0.0067 (2)	0.0030 (1)	0.0006 (2)	0.0016 (1)	−0.0003 (2)
C(3A)	0.3787 (4)	0.1298 (4)	0.2888 (3)	0.0098 (4)	0.0107 (4)	0.0062 (2)	−0.0002 (3)	0.0054 (3)	−0.0016 (3)
N(2)	0.2949 (2)	0.2458 (2)	0.3794 (2)	0.0041 (2)	0.0063 (2)	0.0029 (1)	0.0000 (2)	0.0014 (1)	0.0001 (1)
C(4)	0.3684 (3)	0.3436 (3)	0.3926 (3)	0.0065 (3)	0.0074 (3)	0.0045 (2)	−0.0010 (2)	0.0032 (2)	0.0005 (2)
C(5)	0.3229 (3)	0.4485 (3)	0.4252 (3)	0.0078 (3)	0.0061 (3)	0.0052 (2)	−0.0007 (2)	0.0033 (2)	0.0008 (2)
N(3)	−0.0468 (3)	0.2459 (3)	0.3489 (2)	0.0054 (2)	0.0108 (4)	0.0040 (1)	0.0011 (3)	0.0004 (1)	−0.0018 (2)
O(1)	−0.0369 (3)	0.1415 (4)	0.3496 (3)	0.0104 (3)	0.0110 (4)	0.0105 (3)	−0.0023 (3)	−0.0002 (2)	0.0011 (3)
O(2)	−0.1300 (4)	0.2937 (5)	0.3009 (3)	0.0106 (4)	0.0213 (5)	0.0091 (3)	0.0087 (4)	−0.0046 (3)	−0.0071 (4)
O(3)	0.0300 (4)	0.3005 (4)	0.3975 (3)	0.0093 (4)	0.0134 (4)	0.0126 (4)	0.0000 (4)	−0.0039 (3)	−0.0022 (4)

[a] In this table and those subsequent estimated standard deviations in the least significant figure are given in parentheses. Anisotropic thermal parameters are in the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table III. Bond Lengths (Å) and Angles (deg) for [Ag(*meso*-[14]ane)][NO_3]$_2$

Ag–N(1)	2.162 (3)	C(1)–C(2)	1.544 (5)
Ag–N(2)	2.159 (3)	C(2)–C(3)	1.524 (5)
N(1)–C(1)	1.487 (4)	C(3)–C(3A)	1.527 (5)
N(1)–C(5)′	1.492 (4)	C(4)–C(5)	1.526 (6)
N(2)–C(3)	1.483 (4)	N(3)–O(1)	1.220 (5)
N(2)–C(4)	1.461 (4)	N(3)–O(2)	1.209 (5)
C(1)–C(1A)	1.543 (5)	N(3)–O(3)	1.197 (6)
C(1)–C(1B)	1.528 (5)		

N(1)–Ag–N(2)	95.6 (1)	C(2)–C(3)–C(3A)	110.3 (3)
N(1)–Ag–N(2)′	84.4 (1)	C(2)–C(3)–N(2)	110.2 (3)
N(1)–Ag–O(3)	81.5 (1)	C(3A)–C(3)–N(2)	111.2 (3)
N(2)–Ag–O(3)	94.4 (1)	C(3)–N(2)–Ag	110.6 (2)
Ag–N(1)–C(1)	118.1 (2)	C(3)–N(2)–C(4)	116.2 (3)
C(1)–N(1)–C(5)′	117.7 (2)	Ag–N(2)–C(4)	104.1 (2)
N(1)–C(1)–C(1A)	109.0 (3)	N(2)–C(4)–C(5)	110.2 (3)
N(1)–C(1)–C(1B)	110.6 (3)	C(4)–C(5)–N(1)′	109.7 (3)
N(1)–C(1)–C(2)	109.2 (2)	C(5)–N(1)–Ag	103.7 (2)
C(1A)–C(1)–C(1B)	109.6 (3)	O(1)–N(3)–O(2)	122.2 (4)
C(1A)–C(1)–C(2)	107.5 (3)	O(1)–N(3)–O(3)	117.3 (4)
C(1B)–C(1)–C(2)	110.9 (3)	O(2)–N(3)–O(3)	120.5 (5)
C(1)–C(2)–C(3)	119.4 (3)		

During initial refinement it was observed that the thermal parameters for the nitrate oxygens were unusually large (~8 Å^2). Subsequent examination of a difference Fourier which included all nonhydrogen atoms indicated scattered regions of electron density in the vicinity of the nitrates. Attempts to derive models to describe the disorder were not successful, however. Refinement continued to isotropic convergence at 0.054 and 0.089 where $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

At this point the positions of the hydrogens were obtained from a difference map. These were assigned isotropic temperature factors 1 Å^2 larger than the atom to which they were attached and included as fixed atom contributions. Four cycles of least-squares refinement in which all nonhydrogens were varied anisotropically resulted in anisotropic convergence at $R_1 = 0.033$ and $R_2 = 0.053$. In the last cycle of refinement no atom shifted by more than 0.02 of its esd with the exception of the oxygens for which the largest shift was 0.16. The estimated standard deviation of an observation of unit weight given as $\sigma = [\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$ was 2.05 where $N_o = 2268$, the number of observed reflections, and $N_v = 130$, the number of variable parameters. With the exception of some residual electron density around the nitrates, the final difference map was featureless with a maximum electron density less than 0.7 e/Å.

The final positional and thermal parameters are listed in Table I. Table II, the observed and calculated structure factors, is available as supplementary material. Table III gives interatomic bond lengths and angles for nonhydrogens. Positional and thermal parameters for hydrogens and resulting interatomic distances are found in Tables IV and V in the supplementary material.

Table VI. Selected Least-Squares Planes and Atom Displacements (Å) for [Ag(*meso*-[14]ane)][NO_3]$_2$[a]

Atom	Distance, Å	Atom	Distance, Å
A. Ag–N(1)–C(1)–C(2)–C(3)–N(2)			
$-0.6682x + 0.1802y - 0.7219z = -4.7996$			
Ag*	−0.1424	C(2)*	0.3018
N(1)*	0.1654	C(3)*	−0.3362
C(1)*	−0.2268	C(3A)	−0.1551
C(1A)	0.4416	N(2)*	0.2382
C(1B)	−1.7442		
B. Ag–N(2)–C(4)–C(5)–N(1)			
$-0.7237x + 0.2726y - 0.6340z = -4.0646$			
Ag*	−0.0009	C(5)*	0.3001
N(2)*	0.1513	N(1)′*	0.1513
C(4)*	0.3074		
C. N(3)–O(1)–O(2)–O(3)			
$0.6617x + 0.0598y - 0.7473z = -5.3101$			
N(6)*	−0.0027	O(2)*	0.0009
O(1)*	0.0009	O(3)*	0.0009

[a] Atoms used in the calculation of the plane are denoted by asterisks.

Table VII. Dihedral Angles (deg) for [Ag(*meso*-[14]ane)][NO_3]$_2$

Ag–N(2)–C(3)–C(3A)	−176.3 (2)
Ag–N(2)–C(3)–H(10)	83.3 (3)
Ag–N(1)–C(1)–C(2)	−46.4 (3)
N(1)–C(1)–C(2)–C(3)	70.9 (4)
C(1)–C(2)–C(3)–N(2)	−82.5 (4)
C(2)–C(3)–N(2)–Ag	61.0 (3)
C(3)–N(2)–Ag–N(1)	−38.6 (2)
N(2)–Ag–N(1)–C(1)	33.4 (2)
Ag–N(2)–C(4)–C(5)	−43.8 (3)
N(2)–C(4)–C(5)–N(1)′	59.4 (3)
C(4)–C(5)–N(1)′–Ag	−41.3 (2)
C(5)–N(1)′–Ag–N(2)	104.4 (3)
N(1)′–Ag–N(2)–C(4)	−90.4 (3)

Results and Discussion

As can be seen by the stereoscopic view of [Ag(*meso*-[14]ane)][NO_3]$_2$ in Figure 1, the immediate coordination sphere of the silver is square planar as required by the crystallographic inversion center. The silver is thus incorporated into the plane of the four nitrogen atoms. Weak axial interactions, a characteristic of d^9 systems, are also observed. The two axial coordination sites are occupied by O(3) and O(3)′ at 2.807 (4) Å, and the Ag–O(3) bonds are tilted 9.2° from the normal to the AgN_4 plane, giving a distorted octahedral geometry.

The saturated ligand system consists of two six-membered and two five-membered rings in chair and gauche forms, respectively. The ring conformations can be seen by examination of the deviations from the mean planes (Table VI) and dihedral angles (Table VII) for each ring as well as in the stereoview in Figure 1. Together with the required C_i sym-

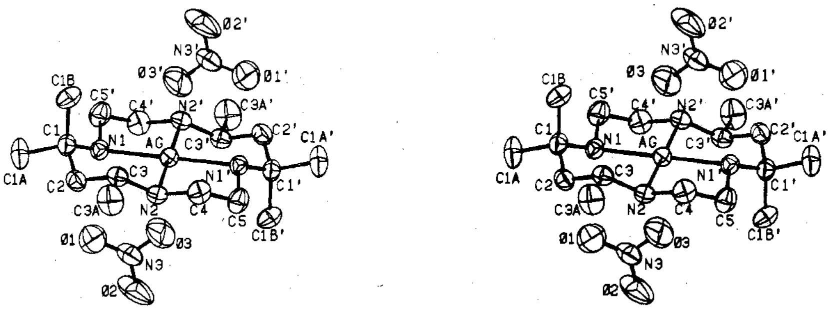

Figure 1. Stereoscopic view of $[Ag(\textit{meso}\text{-}[14]ane)][NO_3]_2$ showing ellipsoids of 50% probability.

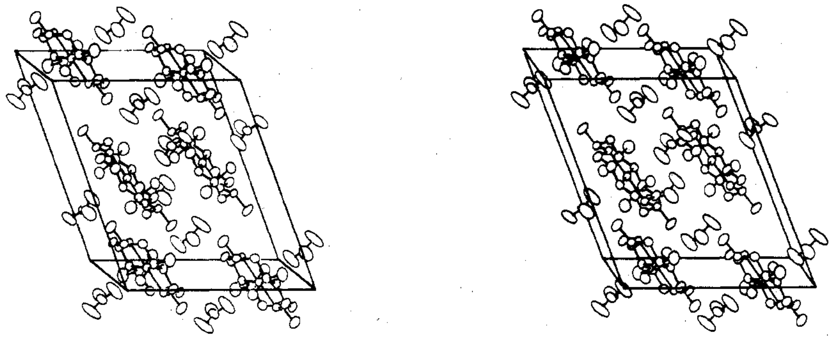

Figure 2. Packing diagram for $[Ag(\textit{meso}\text{-}[14]ane)][NO_3]_2$ as viewed down the *c* axis.

metry and the orientation of the NH groups (in which H(N1) and H(N2) are on the same side of the ring and H(N1)′ and H(N2)′ are related by inversion through the silver), these observations are consistent with two of the ten diastereomers possible for a square-planar complex of the meso form of this ligand.[15] The other differentiating feature which enables the diastereomeric configuration to be assigned unambiguously is the equatorial C(3A) orientation. This can be ascertained from the dihedral angle Ag–N(2)–C(3)–C(3A) of −176.3 (2)°, denoting a nearly parallel orientation of C(3A) with respect to the AgN_4 plane. The Ag–N(2)–C(3)–H(10) angle is 83.3 (2)°, indicating an axial bond. Indeed, the equatorial placement of C(3A) is anticipated considering findings for $[Ni(\textit{meso}\text{-}[14]ane)]^{2+}$ [15] as well as energy calculations which predict this configuration to be energetically more favorable, with fewer nonbonding repulsions.[16]

The bond lengths and angles within the cation are as anticipated. The Ag–N bonds, which average 2.160 (3) Å, are in agreement with previous structural data on covalent Ag–N bonding, where Ag–N, in general, ranges from 2.09 to 2.21 Å.[2,17] The N(1)–Ag–N(2)′ angle is 84.4 (1)°, which is, as expected, smaller than the N(1)–Ag–N(2) angle of 95.6 (3)°. These angles are similar to the corresponding ones on other 14-membered macrocyclic systems.[18–20]

Bond lengths within the macrocyclic rings are indicative of the saturated nature of the ligand system. The internal ring angles also conform to previously reported structural results for similar complexes. Two deviations from "ideal" tetrahedral angles are noted, in particular, which are characteristic of six-membered metal chelate rings. The first of these is the large C(1)–C(2)–C(3) angle of 119.4 (3)°, which is noted for chelate rings in the chair form with three methyl substitutents.[19,21,22,23] The large Ag–N(1)–C(1) angle of 118.1 (2)° is the second feature which $[Ag(\textit{meso}\text{-}[14]ane)]^{2+}$ has in common with other metal chelates. Indeed, this can be seen from structural data on both the meso and rac forms of $[Ni([14]ane)]^{2+}$ where Ni–N–C ranges from 110.8 (8) to 125.2 (6)°.[18,19,23] The opening of the M–N–C angle results from a general flattening of the chelate ring at the silver. The dihedral angles of 33.4 (2)° for N(2)–Ag–N(1)–C(1) and −38.6 (2)° for C(3)–N(2)–Ag–N(1) (Table VII), considerably less than the 60° attributed to an ideal chair conformation, provide additional evidence for the ring leveling.

The nitrates are virtually planar, as seen in Table VI. These planes are tilted from the vertical to the AgN_4 plane by 2.6 (6)° and oriented almost parallel to N(1)–Ag–N(1)′ lying approximately 13° within the six-membered chelate rings (Figure 1). The positioning of the nitrate groups is such that the O(1)–H(N1) distance of 2.308 (4) Å is favorable for hydrogen bonding, and the closest C(1) methyl group is in an equatorial orientation, thus avoiding unnecessary repulsions. The N–O bond lengths, which in nitrates usually vary from 1.22 to 1.27 (±4) Å,[24] average 1.209(5) Å in this complex and thus are somewhat shorter than normal, although still within the standard deviations of the aforementioned range. The O–N–O bond angles averaging 120.0 (4)° are reasonable for trigonal nitrogen.

As mentioned previously, axial interactions are observed between Ag and O(3) and O(3)′ at 2.807 (4) Å. Weak coordination at the fifth and sixth sites for silver(II) has been observed in other nitrate complexes. In bis(2,2′-bipyridine)silver(II) nitrate, $[Ag(bpy)_2][NO_3]_2\cdot H_2O$, the square plane is occupied by the four pyridine nitrogens at an average distance of 2.16 Å while axial interactions with two bridging nitrate groups are found at 2.78 and 2.82 Å.[25] Also, in dinitrato-2,2′-bipyridinesilver(II), the silver shows planar coordination to one bipyridine and two nitrate oxygens, in addition to weak axial interactions at 2.75 and 2.76 Å with neighboring oxygens.[26] Hence, this type of distorted octahedral coordination appears to be particularly characteristic of silver(II) complexes containing nitrate groups.

Because of the presence of amino hydrogens and the close approach of the oxygens to the N_4 plane, it might be anticipated that hydrogen bonding would be present. Indeed, two relatively short O–H distances are apparent: O(1)–H(N1) = 2.308 (4) Å and, for an O(2) from a neighboring nitrate, O(2)–H(N2) = 2.271 (4) Å. The resulting N–O distances and N–H···O angles are N(1)···O(1) = 3.002 (5) and N(2)···O(2) = 2.883 (4) Å and N(1)–H(N1)···O(1) = 158.9 (2)° and N(2)–H(N2)···O(2) = 132.9 (2)°, the latter angle being close to the lower limit usually observed for hydrogen bonding.[27] In this manner a linking through hydrogen bonding of complexes related by the *c* glide occurs throughout the unit cell.

One other structural report of a silver(II) complex with a tetradentate nitrogen donor macrocycle has appeared: a (tetraphenylporphyrin)silver–tetraphenylporphyrin molecular solid solution.[28] This compound was actually a solid solution of the silver and free base porphyrin with the silver occupying the porphinato central hole 54% of the time. The silver and four nitrogens were found to be coplanar with an Ag–N bond length of 2.063 (5) Å. This rather short Ag–N bond length compared to other Ag(II) structures could be an artifact of the disorder but more probably is a consequence of the well-documented propensity of porphyrins to attain a central hole radius of approximately 2.01 Å.[29]

The [Ag(*meso*-[14]ane)][NO_3]$_2$ structure is thus the first reported on a silver(II) macrocyclic complex with a completely saturated nitrogen donor ligand. Weak axial coordination also appears to be characteristic of Ag(II) complexes[17,25,26,30] and is, of course, well documented for Cu(II).[31] Additional silver complexes in various oxidation states are currently being investigated to elucidate further the influence of macrocyclic ligands on coordination and bonding of the silver ion.

Acknowledgment. I wish to thank Professor Reynold T. Iwamoto for a sample of [Ag(*meso*-[14]ane)][NO_3]$_2$ and Professor B. K. Lee for use of his x-ray crystallographic program library. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the University of Kansas General Research Fund, for support of this research.

Registry No. [As(*meso*-[14]ane)][NO_3]$_2$, 64598-79-4.

Supplementary Material Available: Tables II, the structure factor listings, IV, the positional and thermal hydrogen parameters, and V, the interatomic distances involving hydrogens (22 pages). Ordering information is given on any current masthead page.

References and Notes

(1) J. J. Christensen, D. J. Eatough, and R. M. Izatt, *Chem. Rev.*, **74**, 315 (1974).
(2) H. N. Po, *Coord. Chem. Rev.*, **20**, 171 (1976).
(3) G. W. A. Fowles, R. W. Matthews, and R. A. Walton, *J. Chem. Soc. A*, 1108 (1968).
(4) D. P. Murtha and R. A. Walton, *Inorg. Chem.*, **12**, 1278 (1973).
(5) M. O. Kestner and A. L. Allred, *J. Am. Chem. Soc.*, **94**, 7189 (1972).
(6) E. K. Barefield and M. T. Mocella, *Inorg. Chem.*, **12**, 2829 (1973).
(7) Computer programs for the unit cell calculations and collection of data were supplied by Syntex Analytical Instruments.
(8) *P*2$_1$ operations manual.
(9) G. Friedlander and J. W. Kennedy, "Introduction to Radiochemistry", Wiley, New York, N.Y., 1949, p 214.
(10) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).
(11) The programs used were local modifications of A. Zalkin's FORDAP for the Fourier summation, W. Busing, K. Martin, and H. Levy's ORFLS and ORFFE-II for least-squares and function and error calculations, and C. K. Johnson's ORTEP-II for the molecular structure drawing. Computations were performed on the Honeywell 635 and 66/60 computers at the University of Kansas.
(12) D. T. Cromer and J. T. Waber, *Acta Crystallogr., Sect. A*, **18**, 104 (1965).
(13) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).
(14) J. A. Ibers, "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1968, Tables 3.3.1A and 3.3.2C.
(15) L. G. Warner and D. H. Busch, *J. Am. Chem. Soc.*, **91**, 4092 (1969).
(16) L. J. DeHayes and D. H. Busch, *Inorg. Chem.*, **12**, 1505 (1973).
(17) M. G. B. Drew, R. W. Matthews, and R. A. Walton, *J. Chem. Soc. A*, 1405 (1970).
(18) N. F. Curtis, D. A. Swann, and T. N. Waters, *J. Chem. Soc., Dalton Trans.*, 1408 (1973).
(19) N. F. Curtis, D. A. Swann, and T. N. Waters, *J. Chem. Soc., Dalton Trans.*, 1963 (1973).
(20) W. Wagner, M. T. Mocella, M. J. D'Aniello, Jr., A. H.-J. Wang, and E. K. Barefield, *J. Am. Chem. Soc.*, **96**, 2625 (1974).
(21) R. R. Ryan, B. T. Kilbourn, and J. D. Dunitz, *J. Chem. Soc. A*, 2407 (1969).
(22) F. Hanic and M. Serator, *Chem. Zvesti*, **18**, 572 (1964).
(23) P. O. Whimp, M. F. Bailey, and N. F. Curtis, *J. Chem. Soc. A*, 1956 (1970).
(24) H. Ondik and D. Smith, "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1968, Table 4.1.5.
(25) J. L. Atwood, M. L. Simms, and D. A. Zatko, *Cryst. Struct. Commun.*, **2**, 279 (1973).
(26) G. W. Bushnell and M. A. Khan, *Can. J. Chem.*, **50**, 315 (1972).
(27) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids", W. A. Benjamin, New York, N.Y., 1968.
(28) M. L. Schneider, *J. Chem. Soc., Dalton Trans.*, 1093 (1972).
(29) J. L. Hoard, *Science*, **174**, 1295 (1974).
(30) M. G. B. Drew, R. W. Matthews, and R. A. Walton, *Inorg. Nucl. Chem. Lett.*, **6**, 277 (1970).
(31) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Interscience, New York, N.Y., 1972.

Contribution from the Department of Chemistry, Tulane University,
New Orleans, Louisiana 70118

Ligand Lability Studies in Bridging Hydride Complexes of Group 6B Metal Carbonylates

MARCETTA Y. DARENSBOURG,* NYAL WALKER, and ROBERT R. BURCH, JR.

Received April 26, 1977

The reactions of $Et_4N^+\mu\text{-}H[M(CO)_5]_2^-$ (M = Cr, Mo, W) with 5A donor ligands have been studied. The predominant if not exclusive product in all cases studied here is $L_2M(CO)_4$. The reaction follows a rate law that is first order with respect to the concentration of bridging hydride carbonylate and zero order with respect to the 5A donor ligand concentration when the ligand is in a tenfold or greater excess. Rate constants are dependent on metal (Mo > Cr > W) and on solvent (EtOH > THF). It is proposed that initial substitution occurs on the hydride-bridged dimer, prior to dimer disruption. A complex formulated as $Et_4N^+\mu\text{-}H[Mo(CO)_5][Mo(CO)_4PPh_3]^-$ was isolated as the first-formed product in the $Et_4N^+\mu\text{-}H[Mo(CO)_5]_2^-$ reaction with PPh_3 in THF. Rates of reaction of $\mu\text{-}H[M(CO)_5]_2^-$ with L to form $L_2M(CO)_4$ were compared with rates of the nucleophile-facilitated substitution reaction, $NaBH_4/M(CO)_6/L$, also to form $L_2M(CO)_4$ or $L_3M(CO)_3$. The intermediacy of a bridging hydride, $\mu\text{-}H[M(CO)_5]_2^-$, in the sodium borohydride facilitated substitution reactions of $M(CO)_6$ is consistent with the formation of $\mu\text{-}H[M(CO)_5]_2^-$, reaction rates, and products.

Introduction

The nucleophile-facilitated preparation of group 5A donor ligand substituted 6B metal carbonyls or iron carbonyls has been the subject of several reports recently. This interest stems from a need to develop facile or specific syntheses under mild conditions and has the potential of contributing to the challenging area of mechanistic information regarding small molecule or ion loss from low-valent metal complexes. Specifically the reports have included the following. Chatt et al. reported the synthesis of a great number of di- and trisubstituted 6B metal carbonyls as "catalyzed" by sodium borohydride, in refluxing EtOH.[1] Shaw and Hui utilized a

0020-1669/78/1317-0052$01.00/0