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Crystal and Molecular Structure of a 14-π-Electron Macrocyclic Gold(III) Complex

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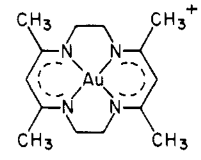
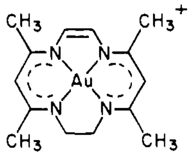
Recent work in this laboratory[1] demonstrated that $[Au(en)_2]Cl_3$ reacts with β-diketones in aqueous base to form 14-membered, tetraaza ring, 12-π-electron macrocyclic cation complexes such as I. The X-ray crystal structure[2] of the chloride salt of I showed the cation to be nearly planar with the gold atom at a crystallographic center of symmetry. Delocalization of π electrons within the six-membered, β-diiminate rings was indicated by the observed pattern of C–C and C–N bond distances.


I


II

Complex II was isolated during efforts[1] to prepare a fully delocalized macrocycle by oxidation of I. So that the effects of additional unsaturation on the structural parameters of the macrocycle could be assessed, a crystallographic structure determination of the BF_4^- salt of II has been carried out. Results of that study are reported here.

Experimental Section

The BF_4^- salt of 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,6,9,11,13-pentaenato gold (III), cation II, was prepared and crystallized as described previously.[1] Precession and Weissenberg film data indicated a triclinic space group. A good-quality crystal was mounted and centered on a Syntex $P2_1$ autodiffractometer, and unit cell dimensions and the orientation matrix were obtained with standard Syntex programs. Data were collected as described previously.[2] The intensities of seven standard reflections, measured after every 200 reflections, showed no evidence for crystal decomposition. Essential data are given in Table I.

The intensity data were corrected for absorption[3,4] and for Lorentz and polarization effects.[5] The structure was solved by the heavy-atom method.[6] The Au atom was located in a three-dimensional Patterson map, and subsequent Fourier syntheses revealed all other nonhydrogen atoms and an inversion center. Refinement of the structure was thus carried out in space group $P\bar{1}$. A difference Fourier synthesis, performed after several cycles of full-matrix, least-squares refinement of heavy-atom positions and anisotropic thermal parameters (isotropic thermal parameters were used for fluorine atoms), revealed all 20 hydrogen atoms. The positions thus found for these atoms were included but not allowed to vary during the final cycles of refinement. The largest shift of any parameter during the last cycle was 51% of σ.[7]

Table I. Summary of Crystallographic Data for (5,7,12,14-Tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,6,9,11,13-pentaenato)gold(III) Tetrafluoroborate

formula	$AuN_4C_{14}H_{20}BF_4$
a, Å	7.344 (1)
b, Å	11.192 (2)
c, Å	11.751 (2)
α, deg	115.62 (1)
β, deg	106.59 (1)
γ, deg	92.04 (1)
V, Å^3	820 (1)
Z	2
space group	$P\bar{1}$
d_{calcd}, g/cm^3	2.14
d_{obsd}, g/cm^3 [a]	2.13
cryst dimens, mm	0.14 × 0.17 × 0.25
cryst faces	(100), ($\bar{1}$00), (010), (0$\bar{1}$0), (001), (00$\bar{1}$), (01$\bar{1}$), (0$\bar{1}$1)
radiatn[b]	Mo Kα (*l* = 0.710 69 Å)
abs coeff (μ), cm^{-1}	93.13
scan rate, deg/min	2.0-29.3 (θ-2θ)
scan range, deg	1.0° below $K\alpha_1$ to 1.0° above $K\alpha_2$
bkgd/scan time ratio	1.0
data collected	2θ of 4.9-42.5°; +*h*,±*k*,±*l*
std reflctns	600, 080, 0011, 7$\bar{2}$0, 504, 0,11,$\bar{7}$, 6$\bar{4}\bar{2}$
no. of independent reflctns collected	1819
no. of reflctns with $I > 3\sigma(I)$ used	1718
error in observn of unit weight	7.6
R	4.6
R_w	7.4

[a] Determined by flotation in $ZnBr_2$ solution at 25 °C.
[b] Graphite-monochromated radiation.

Table II. Final Atomic Positional Parameters[a]

atom	*x*	*y*	*z*
Au	0.1919 (1)	0.4812 (1)	0.4024 (1)
N(1)	0.0448 (24)	0.3461 (18)	0.2170 (18)
N(4)	0.1989 (25)	0.6010 (17)	0.3209 (17)
N(8)	0.3481 (22)	0.6181 (18)	0.5875 (18)
N(11)	0.1837 (22)	0.3621 (18)	0.4858 (17)
C(2)	−0.0115 (37)	0.4063 (26)	0.1308 (23)
C(3)	0.1252 (32)	0.5233 (25)	0.1692 (24)
C(5)	0.2901 (27)	0.7250 (22)	0.3878 (21)
C(5′)	0.2937 (50)	0.8014 (27)	0.3072 (30)
C(6)	0.3792 (29)	0.7932 (22)	0.5306 (26)
C(7)	0.3962 (29)	0.7415 (24)	0.6144 (24)
C(7′)	0.5204 (32)	0.8397 (22)	0.7666 (20)
C(9)	0.3688 (27)	0.5624 (20)	0.6722 (21)
C(10)	0.2894 (18)	0.4339 (13)	0.6219 (13)
C(12)	0.0992 (35)	0.2300 (20)	0.4132 (21)
C(12′)	0.1189 (35)	0.1531 (21)	0.4957 (22)
C(13)	0.0015 (28)	0.1689 (21)	0.2816 (24)
C(14)	−0.0278 (26)	0.2201 (21)	0.1885 (20)
C(14′)	−0.1642 (27)	0.1279 (21)	0.0443 (20)
B	0.6921 (43)	0.7676 (24)	0.1162 (30)
F(1)	0.7707 (36)	0.6791 (26)	0.1565 (25)
F(2)	0.5355 (51)	0.7029 (36)	0.0170 (36)
F(3)	0.8305 (61)	0.8056 (43)	0.0722 (41)
F(4)	0.6647 (36)	0.8745 (27)	0.2086 (26)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Final atomic positions are given in Table II. Bond lengths and angles are listed in Table III. The numbering system is shown in Figure 1.

Results and Discussion

The macrocyclic cation II is very nearly planar. The maximum deviation of any nonhydrogen atom from the least-squares plane of all heavy atoms in the cation is 0.26 (3) Å (C(2)). C(3) is 0.22 (2) Å on the opposite side of this plane, consistent with a slight gauche arrangement of the ethylene

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(1) Kim, J.-H.; Everett, G. W. *Inorg. Chem.* **1979**, *18*, 3145-3149.
(2) Kim, J.-H.; Everett, G. W. *Inorg. Chem.* **1981**, *20*, 853-856.
(3) de Meulenaer, J.; Tompa, H. *Acta Crystallogr.* **1965**, *19*, 1014-1018.
(4) Maximum and minimum transmission coefficients are 0.414 and 0.302, respectively.
(5) Locally written programs were used in data reduction.
(6) Programs used for solution and refinement of the structure are local modifications of FORDAP by A. Zalkin and of ORFLS and ORFFE-II by W. Busing, K. Martin, and H. Levy. C. K. Johnson's ORTEP-II was used for the structural drawing. All computations were carried out on a Honeywell 66/60 computer located on campus.
(7) This occurred for the *y* coordinate of C(9). The value of this parameter oscillated without change in maximum and minimum values over seven cycles of full-matrix least-squares refinement.

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Table III. Bond Lengths and Selected Bond Angles[a]

	Bond Lengths, Å		
Au-N(1)	1.972 (17)	C(5)-C(6)	1.435 (32)
Au-N(4)	1.962 (3)	C(6)-C(7)	1.322 (33)
Au-N(8)	1.991 (4)	C(12)-C(13)	1.338 (22)
Au-N(11)	1.975 (16)	C(13)-C(14)	1.410 (30)
N(1)-C(14)	1.350 (25)	C(2)-C(3)	1.436 (30)
N(4)-C(5)	1.298 (20)	C(9)-C(10)	1.329 (27)
N(8)-C(7)	1.288 (23)	C(5)-C(5′)	1.529 (32)
N(11)-C(12)	1.356 (16)	C(7)-C(7′)	1.592 (20)
N(1)-C(2)	1.421 (28)	C(12)-C(12′)	1.534 (24)
N(4)-C(3)	1.517 (22)	C(14)-C(14′)	1.544 (26)
N(8)-C(9)	1.363 (22)	B-F(1-4)	1.285 (35), 1.293 (27), 1.353 (25), 1.393 (43)
N(11)-C(10)	1.393 (23)		
	Bond Angles, Deg		
N(1)-Au-N(4)	83.6 (5)	C(12)-C(13)-C(14)	129.6 (17)
N(4)-Au-N(8)	95.5 (1)	N(8)-C(9)-C(10)	118.5 (15)
N(8)-Au-N(11)	84.2 (4)	N(11)-C(10)-C(9)	119.2 (17)
N(11)-Au-N(1)	96.8 (6)	N(1)-C(2)-C(3)	112.8 (19)
N(1)-C(14)-C(13)	125.2 (17)	N(4)-C(3)-C(2)	107.9 (16)
N(4)-C(5)-C(6)	123.6 (18)	C(3)-N(4)-C(5)	123.8 (13)
N(8)-C(7)-C(6)	128.6 (19)	C(2)-N(1)-C(14)	125.4 (18)
N(11)-C(12)-C(13)	124.8 (11)	C(9)-N(8)-C(7)	129.5 (12)
C(5)-C(6)-C(7)	127.5 (19)	C(10)-N(11)-C(12)	128.9 (14)

[a] Estimated standard deviations in the least significant digits are given in parentheses.

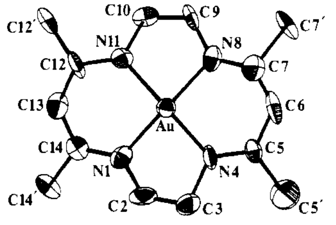

Figure 1. ORTEP drawing of cation II. Thermal ellipsoids are shown at the 50% level.

bridge. The methyl carbons are all within 0.08-0.16 Å of the least-squares plane. The presence of a double bond in one of the five-membered rings is clearly evident from the C(9)-C(10) bond distance of 1.329 (27) Å. Bond distances in the BF_4^- anion vary over a ~0.1 Å range and are shorter than expected.[8] Also the bond angles vary from 102 (2) to 115 (2)°. These deviations from ideal T_d point group symmetry are attributed to the relatively high thermal parameters found for the fluorines.[9]

It is of interest to compare the structural parameters of cation II with those found previously for I. In both complexes, C$\overset{\cdots}{-}$N distances within the *same* β-diiminate ring differ by no more than 0.01 (4) Å. However they differ by as much as 0.07 (4) Å between the two inequivalent β-diiminate rings of II. In one ring, C$\overset{\cdots}{-}$N distances are comparable to those found in I (1.340 (8) Å, average), whereas in the other ring these distances are very close to those found for a β-diimine complex having localized imine double bonds (1.263 (6)-1.282 (7) Å).[10]

The two C$\overset{\cdots}{-}$C distances in I differ only slightly (1.370 (10) and 1.411 (10) Å). In II, on the other hand, differences in the C$\overset{\cdots}{-}$C bond lengths within each β-diiminate ring are significantly greater. This would imply a smaller degree of π delocalization in II; however, the equivalency of C$\overset{\cdots}{-}$N bonds within each ring rules out a structure with alternating double and single bonds. It appears that the presence of the double bond in one of the five-membered rings of II places a steric constraint on the entire macrocycle such that bond lengths cannot be readily interpreted by simple valence-bond considerations.

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Supplementary Material Available: Table IV containing anisotropic thermal parameters and Table V with observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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Structure of a Homoleptic Seven-Coordinate Molybdenum(II) Aryl Isocyanide Complex $[Mo(CNPh)_7](PF_6)_2$[1,2]

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Although the structures of numerous seven-coordinate alkyl isocyanide complexes of divalent group 6 transition metals have been crystallographically determined both in our laboratory[2,3] and in others,[4] no aryl isocyanide complexes have thus far been studied. Recently, homoleptic seven-coordinate aryl isocyanide complexes of Mo(II) and W(II) have become available through the synthetic efforts of Walton and co-workers.[5] A structural study of one of these, $[Mo(CNPh)_7](PF_6)_2$, was therefore undertaken to confirm the proposed coordination number and to provide bond length and angle data for comparison with the known alkyl isocyanide analogues.

Experimental Section

Collection and Reduction of X-ray Data. The synthesis and crystallization of $[Mo(CNPh)_7](PF_6)_2$ have been described previously.[5] The yellow crystal used in the diffraction study had approximate dimensions 0.27 mm × 0.07 mm × 0.47 mm and was sealed in a capillary to minimize decomposition. Study of the compound on the diffractometer showed only $\bar{1}$ Laue symmetry and no systematic absences, indicating either space group $P1$ (C_1^1, No. 1) or $P\bar{1}$ (C_i^1, No. 2).[6] A systematic search using TRACER-II[7] failed to reveal any higher

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(8) MacGillavry, C. H., Rieck, G. D., Eds. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1968; Vol. III, p 262.

(9) Final isotropic thermal parameters for fluorines are as follows: F(1), 11.272 (646); F(2), 15.925 (1025); F(3), 19.922 (1384); F(4), 11.399 (639).

(10) DeHaven, P. W.; Goedken, V. L. *Inorg. Chem.* **1979**, *18*, 827-831.

(1) Part 17 of a continuing series on higher coordinate cyanide and isocyanide complexes. For part 16 see ref 2.

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(4) (a) Brant, P.; Cotton, F. A.; Sekutowski, J. C.; Wood, T. E.; Walton, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 6588. (b) LaRue, W. A.; Liu, A. T.; San Filippo, J. S., Jr. *Inorg. Chem.* **1980**, *19*, 315.

(5) (a) Klendworth, D. D.; Welters, W. W.; Walton, R. A. *J. Organomet. Chem.* **1981**, *213*, C13. (b) Klendworth, D. D.; Welters, W. W.; Walton, R. A., submitted for publication in *Inorg. Chem.*

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