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# Complexes with Macrocyclic Ligands.
# I. The Crystal Structure of a Mercury(II) Chloride Complex of *rac*-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane (tet*b*)

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*A single crystal structure determination was carried out on* $(HgCl_2)_2 \cdot$tet*b*: $Hg_2Cl_4C_{16}H_{36}N_4$, *M = 827.5, a = 18.772(2), b = 10.188(1), c = 13.068(1) Å, β = 101.33(1)°, monoclinic, C2/c, Z = 4,* $D_c$ *= 2.25 g* $cm^{-3}$*, R = 0.047 for 1900 observations with F > 6σ(F). The structural unit is a chloride-bridged species, (tet*b*)Hg(μ-Cl)*$_2$*HgCl*$_2$*, which contains both six- and four-coordinate mercury ions. The complexes lie on crystallographic two-fold axes. The tet*b *ligand is folded so that the four nitrogen atoms occupy adjacent sites on a distorted octahedron; the configuration at each chiral centre is 1S(R), 4S(R), 7R(S), 8S(R), 11S(R), 14R(S). The five- and six-membered rings of the macrocycle are in the gauche and chair forms, respectively. The six-coordinate mercury ions are bonded to two nitrogens at 2.274(7) Å, two nitrogens at 2.440(7) Å, and two chlorides at 2.842(3) Å. The four-coordinate mercury ions are bonded to two bridging chlorides at 2.529(3) Å and two terminal chlorides at 2.421(4) Å.*

## Introduction

Macrocyclic complexes of Hg and Cd are interesting because the multiple donor sites and steric constraints provided by the ligand offer an opportunity to study new and unusual coordination geometries for these elements, and also because macrocycles model ion transport mechanisms in biological systems. We have been exploring complexes with macrocycles having different ring sizes and donor groups. In this paper we report the structure of a mercury chloride compelx of the macrocycle tet*b* (C-*rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) and compare the structure of this complex to structures of other tetraaza macrocycles having a 14-membered ring system.

## Experimental

$(HgCl_2)_2 \cdot$tet*b* was synthesized as follows: $HgCl_2$ (0.20 g, 7.36 X $10^{-4}$ mol) and tet*b* (0.11 g, 3.64 X $10^{-4}$ mol) were each dissolved in 40 ml 1-butanol. The solutions were heated and then stirred together. Slow cooling yielded colourless rectangular or six-sided crystals in 83% yield. *Elemental analyses: Calcd.* for $Hg_2Cl_4C_{16}H_{36}N_4$, 48.48% Hg; 17.14% Cl; 23.22% C; 4.39% H; 6.77% N; *Found*, 49.65% Hg; 17.35% Cl; 23.62% C; 4.54% H; 7.04% N. Analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

A small single crystal (0.06 X 0.10 X 0.28 mm) was mounted on a thin glass fiber with the long axis parallel to the fiber. Oscillation and Weissenberg photographs showed absences consistent with space group *Cc* or *C2/c*. The crystal was transferred to an Enraf-Nonius CAD-4 automated single crystal diffractometer. Graphite-monochromatized Mo-*K*α radiation ($\lambda(\alpha_1)$ = 0.70926 Å) was used to determine the cell dimensions from 25 accurately centered reflections with $15° < \theta < 25°$: *a* = 18.772(2), *b* = 10.188(1), *c* = 13.068(1) Å, β = 101.33(1)°. The data collection conditions were: ω–2θ scan, ω scan width (°) 0.70 + 0.35 tan θ, $\theta_{min} = 2°$, $\theta_{max} = 25°$, 3-mm aperture, maximum ω scan speed 2° $min^{-1}$, maximum scan time 300 s, background counted one quarter of the scan time at each end of the scan. A standard was measured every hour, and the orientation was checked after every 100 measured reflections. The standard decreased slowly during the data collection; its final value was 95% of the initial value. A total of 2320 reflections were measured. Intensities were corrected for background and decrease in the standard, and converted to structure factors after applying Lorentz and polarization corrections. No absorption correction was made ($\mu$ = 13.25 $mm^{-1}$).

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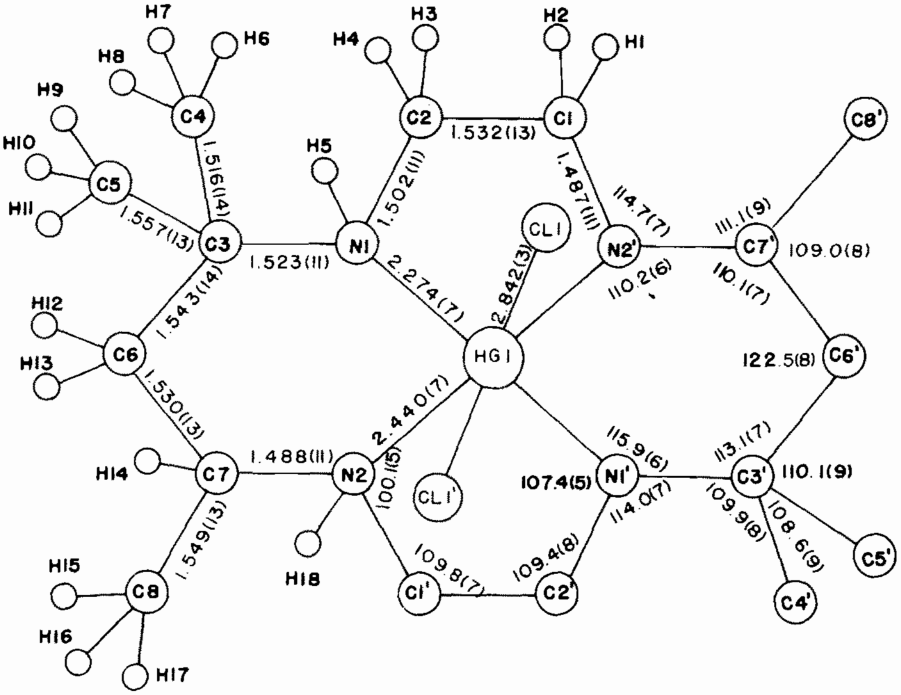


Fig. 1. Selected bond angles and distances in $(HgCl_2)_2\cdot$tet*b*.

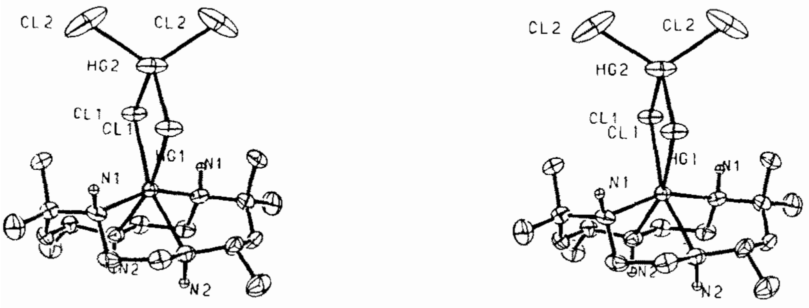


Fig. 2. Stereoview of the $(HgCl_2)_2\cdot$tet*b* complex.

The structure was solved by the heavy atom method and refined by full-matrix least squares techniques with the SHELX set of programs [1]. Scattering factors for neutral C, H, N, Hg, and Cl atoms were taken from International Tables for X-ray Crystallography [2]. The function minimized was $\Sigma w\Delta^2$, where $\Delta = |F_o|-|F_c|$, $F_o$ and $F_c$ are the observed and calculated structure factors, $w = (\sigma^2(F_o) + 0.004\ F_o^2)^{-1}$, and $\sigma(F_o)$ is the standard deviation based on counting statistics. The methyl groups were refined as rigid rotors, and the positions of the remaining hydrogen atoms were calculated. All hydrogen atoms were assigned an isotropic $U$ of 0.06 Å$^2$. The final $R$ and $R_w$ were 0.047 and 0.050, respectively, for the 1900 reflections having $F > 6\sigma(F)$, and 0.057 and 0.055 for all 2161 reflections. The final difference map had a peak about 3e/Å$^3$ near the mercury atom but no other features of note.

The numbering scheme for the macrocycle and most of the bond distances and angles are shown in Fig. 1. The atomic positional and thermal parameters are reported in Tables I and II. Table III contains bond distances and angles not shown in Fig. 1. Figure 2 is a stereo view of the complex, and Fig. 3 shows the packing diagram [3].

## Results and Discussion

The structure contains two different kinds of mercury atoms, each of which lies on a crystallographic two-fold axis. They are linked in pairs by the bridging Cl(1) atoms (Fig. 2). The coordination

TABLE I. Atomic Parameters in $(HgCl_2)_2 \cdot$tet*b*. (E.s.d. s in parentheses).

| Atom | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Hg(1) | 0.5000(0) | 0.84260(5) | 0.2500(0) | 0.0304(3) | 0.0215(3) | 0.0315(3) | 0.0000(0) | 0.0079(2) | 0.0000(0) |
| Hg(2) | 0.5000(0) | 1.22058(6) | 0.2500(0) | 0.0961(6) | 0.0236(4) | 0.0699(5) | 0.0000(0) | 0.0047(4) | 0.0000(0) |
| Cl(1) | 0.5435(2) | 1.0530(2) | 0.3911(2) | 0.071(2) | 0.023(1) | 0.037(1) | −0.001(1) | 0.011(1) | 0.0000(9) |
| Cl(2) | 0.6052(3) | 1.3502(4) | 0.2335(4) | 0.153(4) | 0.087(3) | 0.078(3) | −0.080(3) | −0.021(3) | 0.027(2) |
| N(1) | 0.4270(4) | 0.7972(7) | 0.3653(6) | 0.039(4) | 0.024(4) | 0.035(4) | −0.005(3) | 0.007(3) | −0.001(3) |
| N(2) | 0.4299(4) | 0.6725(8) | 0.1436(6) | 0.038(4) | 0.029(5) | 0.038(4) | −0.004(3) | 0.001(3) | −0.002(3) |
| C(1) | 0.5390(5) | 0.6827(11) | 0.4523(7) | 0.047(5) | 0.039(6) | 0.026(4) | 0.004(4) | 0.000(4) | 0.000(4) |
| C(2) | 0.4559(5) | 0.6752(9) | 0.4234(7) | 0.052(6) | 0.032(5) | 0.035(5) | −0.001(4) | 0.015(4) | 0.011(4) |
| C(3) | 0.3457(5) | 0.7930(10) | 0.3202(8) | 0.036(4) | 0.031(5) | 0.047(5) | 0.005(4) | 0.006(4) | 0.006(4) |
| C(4) | 0.3042(6) | 0.7658(14) | 0.4063(10) | 0.050(6) | 0.063(8) | 0.059(7) | −0.002(6) | 0.024(5) | 0.002(6) |
| C(5) | 0.3264(6) | 0.9337(10) | 0.2771(11) | 0.046(6) | 0.029(6) | 0.081(8) | 0.013(5) | 0.016(6) | 0.006(6) |
| C(6) | 0.3252(5) | 0.6912(10) | 0.2320(8) | 0.030(4) | 0.032(5) | 0.051(6) | −0.011(4) | 0.005(4) | −0.002(5) |
| C(7) | 0.3508(5) | 0.7021(10) | 0.1281(8) | 0.031(4) | 0.034(5) | 0.043(5) | −0.006(4) | −0.004(4) | 0.002(5) |
| C(8) | 0.3059(6) | 0.6066(12) | 0.0485(9) | 0.055(6) | 0.053(7) | 0.049(6) | −0.014(6) | −0.012(5) | −0.007(6) |

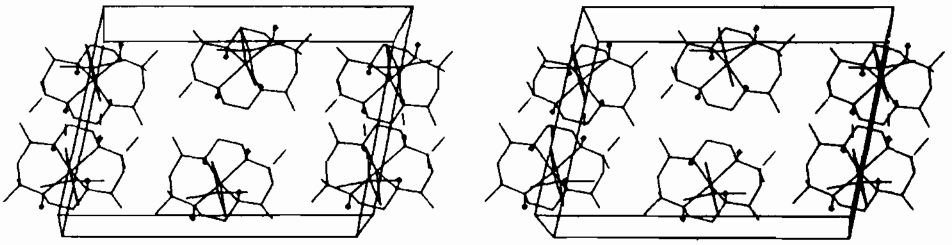


Fig. 3. Molecular packing in $(HgCl_2)_2 \cdot$tet*b*. The view is down the *b*-axis with the *a*-axis horizontal and the *c*-axis vertical.

about the Hg(1) atom can be described as distorted octahedral, with significant deviations from the ideal geometry. Four of the octahedral sites are occupied by the macrocycle nitrogen atoms and two by chlorine atoms Cl(1) and Cl(1)$^i$, where the superscript i refers to an atom symmetry-transformed by the two-fold axis. Bonding of the macrocycle is accomplished by folding along the N(1)···N(1)$^i$ line. This places N(1) and N(1)$^i$ in *trans*-positions, and N(2) and N(2)$^i$ in *cis*-positions on the octahedron, leaving the bridging chlorine atoms to occupy the remaining *cis*-positions. Surprisingly, the distance from Hg(1) to the *trans*-nitrogen atoms N(1) and N(1)$^i$ is considerably shorter (2.274(7) Å) than the distance to the *cis*-nitrogens (2.440(7) Å). Overall, these bond lengths are similar to the ones observed in $[Hg(cyclam)Cl]_2HgCl_4$ [4], although the different configuration of this complex precludes direct comparison (cyclam = 1,4,8,11-tetraazacyclotetradecane).

The Hg(1) surroundings exhibit several deviations from ideal octahedral geometry. The *trans*-angles, N(1)–Hg(1)–N(1)$^i$ and Cl(1)–Hg(1)–N(2), are 156.5(3) and 163.8(2)°, and the intrachelate N–Hg–N ring angles are 78.8(3) and 84.6(3)° for the 5- and 6-membered rings, respectively. The Cl(1)–Hg–Cl(1)$^i$ angle is only 82.0(1)°. The Cl(1)–Hg–Cl(1)$^i$ plane is twisted at a 23° angle with respect to the N(2)–Hg–N(2)$^i$ plane, as shown

TABLE II. Positional Parameters for Hydrogen Atoms in $(HgCl_2)_2 \cdot$tet*b*.

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| H(1) | 0.559 | 0.602 | 0.504 |
| H(2) | 0.554 | 0.774 | 0.490 |
| H(3) | 0.434 | 0.667 | 0.494 |
| H(4) | 0.440 | 0.590 | 0.375 |
| H(5) | 0.430 | 0.879 | 0.418 |
| H(6) | 0.246 | 0.766 | 0.385 |
| H(7) | 0.322 | 0.834 | 0.470 |
| H(8) | 0.323 | 0.668 | 0.430 |
| H(9) | 0.268 | 0.932 | 0.253 |
| H(10) | 0.351 | 0.941 | 0.209 |
| H(11) | 0.342 | 1.017 | 0.327 |
| H(12) | 0.266 | 0.689 | 0.213 |
| H(13) | 0.345 | 0.598 | 0.265 |
| H(14) | 0.343 | 0.801 | 0.098 |
| H(15) | 0.323 | 0.608 | −0.026 |
| H(16) | 0.249 | 0.635 | 0.038 |
| H(17) | 0.313 | 0.509 | 0.081 |
| H(18) | 0.433 | 0.574 | 0.176 |

TABLE III. Selected Distances and Angles in $(HgCl_2)_2 \cdot$tet*b*.

| | | | |
|---|---|---|---|
| | Distances (Å) | | |
| Hg(2)–Cl(1) | 2.529(3) | Hg(2)–Cl(2) | 2.421(4) |
| | Angles (°) | | |
| N(1)–Hg(1)–N(2) | 84.6(3) | Cl(1)–Hg(2)–Cl(1)$^{i}$ | 95.0(1) |
| N(1)–Hg(1)–N(2)$^{i}$ | 78.8(3) | Cl(2)–Hg(2)–Cl(2)$^{i}$ | 113.8(3) |
| N(2)–Hg(1)–N(2)$^{i}$ | 89.4(3) | Cl(1)–Hg(2)–Cl(2) | 106.4(1) |
| N(1)–Hg(1)–N(1)$^{i}$ | 156.5(3) | Cl(1)–Hg(2)–Cl(2)$^{i}$ | 117.1(1) |
| Cl(1)–Hg(1)–Cl(1)$^{i}$ | 82.0(1) | Hg(1)–Cl(1)–Hg(2) | 91.5(1) |
| Cl(1)–Hg(1)–N(2) | 163.8(2) | | |
| Cl(1)–Hg(1)–N(1) | 81.8(2) | N(1)–C(3)–C(5) | 105.0(7) |
| Cl(1)–Hg(1)–N(1)$^{i}$ | 116.7(2) | C(4)–C(3)–C(6) | 110.0(8) |
| N(2)–Hg(1)–Cl(1)$^{i}$ | 96.5(2) | | |

TABLE IV. Least Squares Planes and Deviations (in Å). Asterisks Designate Atoms Used in the Calculation of the Plane.

| | | | |
|---|---|---|---|
| Plane 1: $-0.3548X - 0.7004Y - 0.6194Z = -11.099^{a}$ | | | |
| Hg(1)* | 0.000(1) | C(1) | 0.538(10) |
| N(1)* | 0.000(7) | C(2) | −0.278(9) |
| N(2)$^{i}$* | 0.000(8) | | |
| Plane 2: $0.1769X + 0.9221Y - 0.3443Z = 7.090$ | | | |
| N(1)* | −0.041(7) | C(7)* | −0.050(10) |
| N(2)* | 0.042(8) | Hg(1) | −1.271(1) |
| C(3)* | 0.049(10) | C(6) | 0.644(10) |

[a] X, Y, and Z are orthogonal coordinates, in Å, in a system which has the *x*, *y*, and *z* axes parallel to *a**, *b*, and *c*, respectively.

schematically in Fig. 1. Also, the Hg(1)–Cl(1) bond, 2.842(3) Å, is longer than normal; compare to 2.46(5) Å in $[Hg(cyclam)Cl]^+$ [4] or to the Hg(2)–Cl distances in the present structure. This suggests that the structure could be viewed as a $[($tet*b*$)Hg]^{2+}$ cation interacting weakly with an $[HgCl_4]^{2-}$ anion. The Hg(1)···Hg(2) distance is 3.852(1) Å, a little more than twice the recommended van der Waals radius for mercury of 1.73 Å [5].

The Hg(2) atom is tetrahedrally coordinated to four chlorine atoms, as shown in Fig. 2. The distance from Hg(2) to the nonbridging Cl(2) atoms (2.421(4) Å), is somewhat less than the distance to the bridging Cl(1) atoms (2.529(3) Å). Differences of this magnitude are usually observed when bonds to bridging and nonbridging ligands of the same type are compared. The angles about Hg(2) vary somewhat from the ideal tetrahedral value, but this is principally due to the constraints imposed by the four-membered Hg(1)–Cl(1)–Hg(2)–Cl(1)$^{i}$ ring (Cl(1)–Hg(2)–Cl(1)$^{i}$ = 95.0(1)°).

Least-squares planes for selected groups of atoms are given in Table IV. The deviations of C(1) and C(2) from the N(1)–Hg(1)–N(2)$^{i}$ plane show that the five-membered ring is in the expected *gauche* form. Similarly, the deviations of Hg(1) and C(6) from the N(1)–N(2)–C(3)–C(7) plane show that the six-membered ring is in the chair form. The overall conformation of the tet*b* ligand is similar to that observed for the free ligand [6] and for the nickel and cobalt(II) complexes of tet*b* [7–9], and is discussed further below, where the structural data are compared for cyclam-type complexes.

The molecular packing arrangement is displayed in Fig. 3. There are weak hydrogen bonds from the NH groups to the chloride ligands (Table V) [10]. The N(1)–H(5) groups are donors to the bridging chlorides Cl(1) in centrosymmetrically related mole-

TABLE V. Hydrogen Bonds in $(HgCl_2)_2 \cdot$tet*b*.

| A–H···B | A···B, Å | H···B, Å | A–H···B, ° |
|---|---|---|---|
| N(1)–H(5)···Cl(1)$^{ii}$ | 3.476(8) | 2.537(8) | 144.8(7) |
| N(2)–H(18)···Cl(2)$^{iii}$ | 3.771(9) | 2.734(9) | 160.2(7) |

*Symmetry superscripts*: (ii) $1 - x, 1 - y, 1 - z$; (iii) $1 - x, -1 + y, 0.5 - z$.

TABLE VI. Macrocycle Configuration for Cyclam-type Complexes.

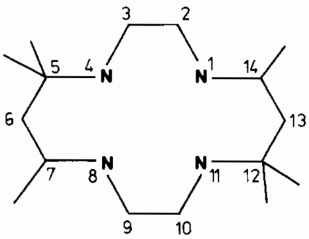
| Complex | *D* (Å) | *Trans* N–N (Å) |  | *Cis* N–N (Å) |  |  |  | Config. at Chiral Atoms |  |  |  |  | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  | N1–N8 | N4–N11 | N1–N4 | N4–N8 | N8–N11 | N11–N1 | N1 | N4 | N8 | N11 | Other |  |
| [Co(cyclam)(en)]$^{3+}$ (*1*) | ±0.61 | 2.970 | 3.988 | 2.698 | 2.833 | 2.702 | 2.832 | R | R | R | R |  | [15] |
| [Pb(cyclam)($NO_3$)$_2$] (*2*) | ±0.42 | 3.262 | 4.662 | 2.863 | 3.057 | 2.925 | 3.041 | R | R | R | R |  | [13] |
| [Hg(cyclam)Cl]$^+$ (*3*) | ±0.20 | 4.365 | 4.503 | 3.099 | 3.185 | 3.160 | 3.203 | R | S | R | S |  | [4] |
| [Fe(NMe$_4$cyclam)NO]$^{2+}$ (*4*) | ±0.18 | 4.122 | 4.318 | 2.883 | 3.118 | 2.875 | 3.142 | R | S | R | S |  | [14] |
| [Ni(tet*a*)(acac)]$^+$ (*5*) | ±0.66 | 3.030 | 4.212 | 2.840 | 2.975 | 2.845 | 3.019 | R | R | R | R | 7R, 14S | [11] |
| [Cu(tet*b*)L]$^+$ (*6*) | ±0.58 | 4.009 | 3.397 | 2.970 | 2.939 | 2.820 | 2.966 | R | R | R | R | 7R, 14R | [12] |
| tet*b*·$H_2O$ (*7*) | ±0.66 | 3.540 | 3.897 | 2.915 | 2.967 | 2.901 | 2.989 |  |  |  |  | 7S, 14S | [6] |
| [Ni(tet*b*)OAc]$^+$ (*8*) | ±0.61 | 3.302 | 4.292 | 2.873 | 3.060 | 2.895 | 3.038 | R | R | R | R | 7S, 14S | [7] |
| [Co(tet*b*)M] (*9*) | ±0.58 | 3.292 | 4.297 | 2.886 | 3.018 | 2.853 | 3.032 | R | R | R | R | 7S, 14S | [9] |
| [{Ni(tet*b*)}$_2$(d-tart)($H_2O$)]$^{2+}$ (*10*) | ±0.59 | 3.282 | 4.277 | 2.830 | 3.043 | 2.841 | 3.044 | R | R | R | R | 7S, 14S | [8] |
|  | ±0.58 | 3.214 | 4.300 | 2.870 | 2.974 | 2.872 | 2.976 | R | R | R | R | 7S, 14S | [8] |
| Hg(tet*b*)($\mu$-Cl)$_2$)HgCl$_2$ (*11*) | ±0.63 | 3.432 | 4.453 | 2.993 | 3.174 | 2.993 | 3.174 | R | R | R | R | 7S, 14S | this work |

Abbreviations: cyclam = 1,4,8,11-tetraazacyclotetradecane; NMe$_4$cyclam = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane; *teta* = *C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; L = *o*-mercaptobenzoate; M = 2,2'-dithiodibenzoate.

cules. The molecules are linked in chains parallel to the y-axis by N(2)–H(18) hydrogen bonds to the terminal chlorides in adjacent molecules one unit cell up or down.

### *Comparison with Other Saturated Tetraaza Macrocycles*

The Cambridge Crystallographic Data Base, as implemented by the Canadian Institute for Scientific and Technical Information at the National Research Council in Ottawa, was used to analyze the geometries of compounds containing a tetraazacyclotetradecane ring. More than 30 structures were located in the search [4, 6–9, 11–40], including one cyclic peptide which models the naturally occurring antibiotic serratamolide [40]. Of these structures, about a third contain the macrocycle in the nonplanar configuration [4, 6–9, 11–16]. It is instructive to compare some of the structural parameters for these compounds. Table VI gives, for all the nonplanar macrocycles, the average deviation *D* of atoms N1, N4, N8, and N11 from the best plane through these atoms, distances between nitrogens *cis* and *trans* to each other in the ring, and the configurations at the chiral centers. These quantities were chosen rather than the torsion angles to describe the structures because they permit ready visualization of the extent of nonplanarity and the cavity size. The atoms in all compounds have been numbered to correspond to the IUPAC system:



One thing which is obvious from Table VI is the predominance of the RRRR configuration at the four nitrogen donor atoms, which is expected for cyclam, tet*a*, and tet*b* in folded conformations [7]. The RSRS configuration is found in only two of the complexes, *3* and *4*, both of which contain five-coordinate metal atoms. The question of whether the configuration determines the metal coordination number or *vice versa* is a moot point. Alcock [4] suggested that the RSRS configuration is favored when the metal ion is too large for the cavity, but the fact that tet*b* adopts the RRRR configuration in the present mercury complex and cyclam takes the RSRS configuration in the iron complex shows that there is no simple correlation between the metal ion size and the ligand configuration.

The macrocycles fold along the N4–N11 line in all tet*a* and tet*b* complexes except 6. The quantity

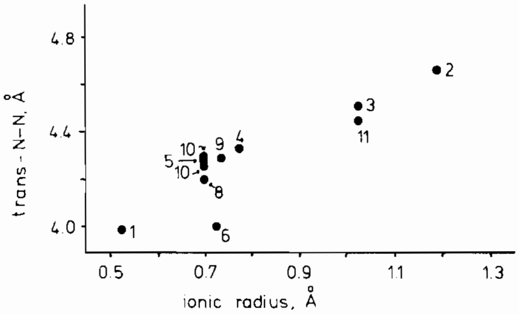


Fig. 4. The macrocycle cavity size as a function of ionic radius of the metal.

*D* is a measure of the extent of folding: *D* is zero or nearly so when the macrocycle coordinates in a square planar fashion, and increases as half of the macrocycle folds towards the other half. The nonplanarity is not directly correlated to metal ion size, as the *D* values are similar for the $Ni^{2+}$ and $Hg^{2+}$ complexes of tet*b* (0.61 and 0.63 Å, respectively), even though $Hg^{2+}$ has a much larger radius than $Ni^{2+}$ (1.02 *vs.* 0.70 Å [41]).

There is a good correlation across the entire series of compounds between the longest *trans* N–N distance and the Shannon and Prewitt ionic radius of the metal [41], as shown in Fig. 4. The *cis* N–N 'bite' distances are not nearly as well correlated. The bite appears to depend at least as much on the ring substituents as on the metal ion size, as may be seen by comparing complex *5* with *8* and *10* or *3* with *11*. It is interesting that the cavity can be opened up along the fold line without corresponding changes in the bites. More structures are needed before a clear picture can be constructed of the changes which occur as a macrocycle accommodates metal ions of different sizes.

We are continuing our work with other macrocyclic complexes of cadmium and mercury, and will soon report the structures of the 18-crown-6 complexes of $CdCl_2$ and $HgCl_2$ [42].

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