Table VI. Important Intramolecular Distances (Å) and Angles (deg) with Esd's[a] for the Species $[(\eta^5\text{-}C_5Me_5)RhX]_2(\mu\text{-}X)_2$ (X = Cl, Br, I)

	$[RhCl]_2\text{-}(\mu\text{-}Cl)_2$[b]	$[RhBr]_2\text{-}(\mu\text{-}Br)_2$[c]	$[RhI]_2\text{-}(\mu\text{-}I)_2$
Rh···Rh	3.719 (1)	3.848 [9]	4.132 (0)
Rh–X(T)	2.397 (1)	2.528 [6]	2.706 (0)
Rh–X(B)	2.459 [9]	2.576 [9]	2.741 (0)
X···X	3.217 (2)	3.427 [15]	3.604 (0)
Rh–X(B)–Rh′	98.29 (3)	96.62 [11]	97.80 (1)
X(B)–Rh–X(B)′	81.71 (3)	83.38 (3)	82.20 (1)
X(B)–Rh–X(T)	91.51 [111]	91.16 [88]	93.29 (1)
Rh–C(ring)	2.126 [11]	2.146 [15]	2.168 [8]
Rh–Cp[d]	1.7558 (3)	1.7691 [3]	1.7792 (3)
Rh···C(Me)	3.256 [24]	3.280 [24]	3.307 [4]
r(X)[e]	0.99	1.14	1.33

[a] Esd's on individual distances or angles are enclosed in parentheses. Esd's on average distances, enclosed in brackets, are calculated by using the "scatter formula" $[\sigma] = [\Sigma(d_i - \bar{d})^2/(N-1)]^{1/2}$. Here d_i is the ith of N equivalent distances and $\bar{d}$ is the average distance. Note that this result provides the "scatter" of values about the average value–i.e., it is an external estimate of the esd on an individual value. The precision of determination of the average value is given by $[\Sigma(d_i - \bar{d})^2/N(N-1)]^{1/2}$. [b] See ref 3. [c] See ref 4. [d] Rh–Cp is the perpendicular distance from the rhodium atom to the pentaatomic carbocyclic ring. [e] These are the covalent radii, taken from: Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, N.Y., 1960; p 224.

(3) The suggested covalent radius for Rh(III), as a mean of $\{d(\text{Rh–X(T)}) - r(\text{X})\}$ is 1.39 Å.

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Registry No. $[(\eta^5\text{-}C_5Me_5)RhI]_2(\mu\text{-}I)_2\cdot 2C_6H_5Me$, 71049-91-7.

Supplementary Material Available: A table of data-processing formulas and a list of structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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Macrocyclic Ligand Synthesis. Isolation of a Dicarbinolamine Complex from a Zinc(II)-Promoted Cyclization Reaction

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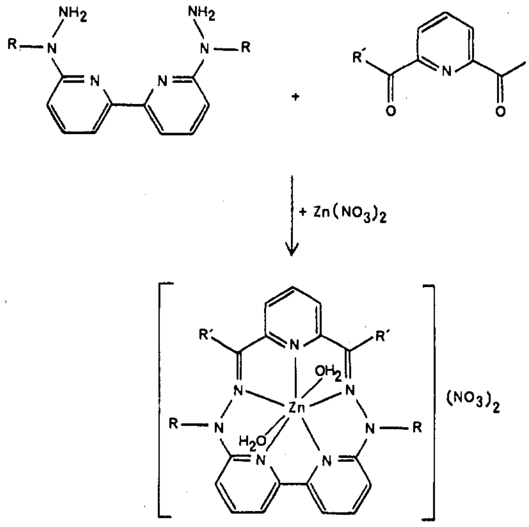
Metal ion "template" assistance in the synthesis of macrocyclic ligands is well documented.[1] Many such syntheses involve the condensation of primary amines with carbonyl-containing functional groups to give macrocyclic imines in which the "template" ion is found coordinated to the imine. Such reactions are presumed to proceed via carbinolamine intermediates,[2] but little is known of the mode of coordination of such intermediates with the metal ion "template".

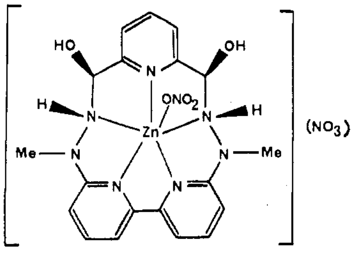
We report here the isolation of a zinc complex of a dicarbinolamine which appears to be an intermediate in the formation of the macrocyclic complex **1a**. It has been demonstrated previously[3] that the macrocycle in **1b** presents a very nearly planar "N_5" donor set to the complexed zinc(II) ion. NMR data[4] and anomalous N–N bond lengths for this compound suggested extensive π delocalization in the macrocycle and led us to attempt the structure determination of the N-methylated compound **1a**. An attempt to grow crystals of **1a** by allowing the reaction to proceed in a large volume of ethanol at room temperature resulted in yellow prisms of {2,6-dihydroxy-8,15-dimethyltripyrido[*c,d:i,j:l,m*][1,4,7,8,-10,13,15]heptaaza[1,2,6,7,8,15]hexahydrocyclopentadecine-$N^1,N^{2b},N^7,N^{8b},N^{12b}$}nitratozinc(II) nitrate (**2**). Longer reaction times and reducing the volume of solvent give in addition to **2** a second product which is assumed to be **1a** on the basis of analytical data[5] and a comparison of IR spectral data with those of the previously characterized complexes **1b** and **1c**.



(1a) R = Me R′ = H

(1b) R = H R′ = Me

(1c) R = H R′ = H



(2)

An X-ray structure determination of **2** was accomplished by using 3185 independent reflections with $I/\sigma(I) \geq 3$ and $3 < \theta < 27°$ obtained on a Philips PW1100 automatic diffractometer with graphite-monochromatized Mo Kα radiation (λ 0.71069 Å). Crystals of **2** ($ZnC_{19}H_{21}N_9O_8$, mol wt 568.8) were triclinic with space group $P\bar{1}$, a = 12.015 (3) Å, b = 10.646 (2) Å, c = 10.434 (2) Å, α = 108.23 (2)°, β = 113.04 (2)°, γ = 78.92 (2)°, U = 1163 Å^3, D_m = 1.60 g cm^{-3}, D_c = 1.62 g cm^{-3}, and Z = 2. Full-matrix least-squares refinement[6] of atomic parameters (Zn, nitrate, and coordinated N atoms anisotropic) gave R_1 = 0.0580 and R_2 = 0.0584.

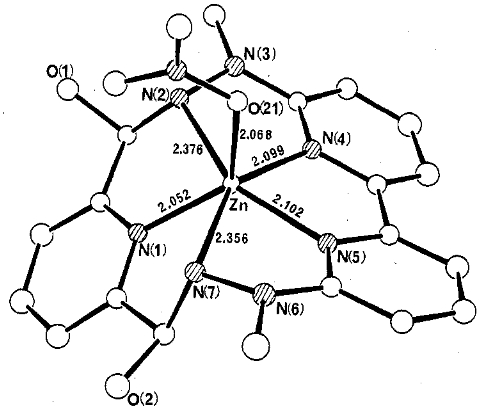


Figure 1. Structure of the monocation of **2**. The mean esd for the bond lengths shown is 0.004 Å. Bond angles (deg) in the coordination sphere (mean esd 0.2°) defined by pairs of donor atoms are N(1),N(2) = 74.3, N(1),N(4) = 123.4, N(1),N(5) = 121.4, N(1),N(7) = 76.0, N(1),O(21) = 126.5, N(2),N(4) = 71.5, N(2),N(5) = 146.6, N(2),N(7) = 141.1, N(2),O(21) = 88.1, N(4),N(5) = 76.1, N(4),N(7) = 147.7, N(4),O(21) = 95.5, N(5),N(7) = 71.6, N(5),O(21) = 101.1, and N(7),O(21) = 89.9°.

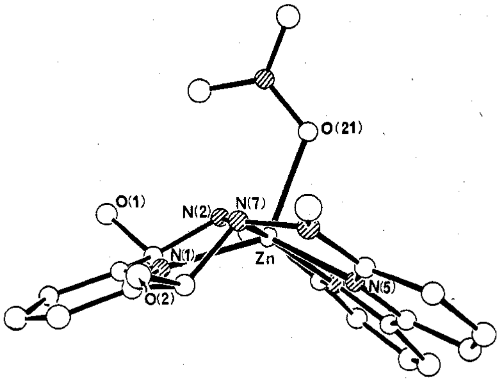


Figure 2. The "folding" of the macrocycle about a line through the carbinolamine nitrogen atoms N(2) and N(7).

The structure determination confirmed the presence of a quinquedenate macrocyclic ligand, in which the expected nitrogen atoms are coordinated to the zinc(II) ion (Figure 1), and showed that the carbinolamine C–O and N–H bonds are all displaced to the same side of the macrocycle. Such a meso arrangement allows the macrocycle to fold about a line through the carbinolamine nitrogen atoms so that the N(1), N(2), N(7) plane is inclined at 64° to the coordination plane defined by the bipyridyl unit (Figure 2).

The isolation of **2** suggests that the formation of **1a–c** (and possibly other complexes of planar conjugated macrocycles) may proceed by formation of a dicarbinolamine before any elimination of water occurs. This might be expected when the ligand precursors are both relatively rigid, because the cyclization step becomes less favorable once one imine bond has formed, since the approach of the second amine nitrogen atom on a line perpendicular to the carbonyl group becomes less probable. Molecular models show that such an effect will be particularly significant when the macrocyclic product has an unstrained planar inner great ring.

In only one case previously[7] has an X-ray structure been reported for a metal complex of a carbinolamine ligand, although such complexes are implicated[8] in a number of metal-catalyzed and enzymatic reactions. Closely related compounds which contain α-amino ether groups are more common.[9] The stability of **2** can be ascribed partly to the extensive inter- and intramolecular H bonding between hydroxyl groups and nitrate ions and partly to the ability of zinc(II) ions to form strong bonds to nitrogen and oxygen donors even in very irregular coordination polyhedra (see Figure 1). Such properties are assumed to be important in a number of other reactions[10] which are promoted by zinc(II) ions.

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Registry No. **2**, 71171-43-2.

Supplementary Material Available: A listing of structure factor amplitudes for **2** (19 pages). Ordering information is given on any current masthead page.

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A Convenient Synthesis and Vibrational Spectrum of Tellurium Bromide Pentafluoride

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Tellurium pentafluoride ($TeBrF_5$) was first prepared in low yield by Fraser, Peacock, and Watkins[1] by the reaction of fluorine and tellurium tetrabromide. Large amounts of tellurium hexafluoride and bromine were also produced from which the product was not separated. We wish to report a convenient synthesis of $TeBrF_5$ in good yield, by the reaction of bromine, fluorine, and tellurium tetrafluoride. The vibrational spectrum was obtained and assigned by comparison with related molecules.

Experimental Section

Techniques and apparatus are described in ref 2. Sodium fluoride, TeO_2, and SF_4 were used without further purification. Fluorine (Matheson) was stored over NaF to remove HF. Bromine (McArthur Chemical Co.) was dried over P_2O_5. Tellurium tetrafluoride was prepared by the reaction of TeO_2 with SF_4 and resublimed before use.[3]

Infrared spectra were recorded on a Perkin-Elmer 467 spectrometer in the range of 4000–250 cm^{-1}. Stainless steel cells of 10-cm path length fitted with AgCl windows and a glass cell fitted with polyethylene windows were used as sample containers. Samples of liquid $TeBrF_5$ for Raman spectroscopy were prepared by condensing $TeBrF_5$ into glass capillary tubes which were then vacuum sealed. Raman