h. After 4 h the solid product was isolated by filtration, washed with petroleum ether, and dried in vacuo to give 70 mg (66%) of $Rh_2(\mu\text{-}CCH(Ph))(CO)_2(\mu\text{-dppm})_2$ (**5**). The complex was characterized by comparison of its spectral data (^1H and ^{31}P NMR and IR) and unit cell constants (X-ray) with literature values.[19]

Structure Analyses. An outline of crystallographic and data collection parameters is given in Table III. Crystals of **2** (dppm, R = Me) were grown by allowing a concentrated solution of the complex to stand (under N_2) in toluene for 12 h. A crystal was selected and mounted on the end of a glass fiber in air. Crystals of **1** (dppm, R = $p\text{-}NO_2Ph$) were grown by slow diffusion of Et_2O into a solution of the complex in CH_2Cl_2. An air-stable needle was cut to size and mounted on the end of a glass fiber. Crystals of $Rh_2(\mu\text{-}O)(CO)_2(\mu\text{-dppm})_2$ (**4**) (see Results) were grown by slow diffusion of ether into a toluene solution of **1**/**2** (dppm, R = Ph). A crystal was selected and mounted in air on the end of a glass fiber.

Cell dimensions were based upon Delaunay reductions of cells obtained from the centering of 25 reflections on the diffractometer. Intensity data (294 K) were collected with Mo Kα radiation from a graphite monochromator (θ–2θ scan, 96 steps/scan, 16 steps/side background). The intensities of three standard reflections were measured after each 7200-s exposure to the X-rays and were used to correct for any decay of intensity during the course of the experiment. Empirical absorption corrections were applied as needed based on ψ scans. The Enraf-Nonius SDP program package was used for all calculations. The structures were resolved by Patterson or direct methods followed by successive applications of Fourier methods. Phenyl and methylene hydrogen atoms were placed in calculated fixed positions. Full-matrix least-squares refinement minimizing $\sum w(|F_o| - |F_c|)$ converged to the R values given in Table III. No extinction corrections were applied. Two unresolved disordered toluene molecules, well separated from the A-frame molecule, were included in the structure of **2**. Selected bond distances and angles are given in Tables IV–VI. Other data are included as supplementary material.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, ARCO Chemical Co., and the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy (Contract DE-FG02-88ER13880) for support of this work. A loan of $RhCl_3$ and $IrCl_3$ from Johnson Matthey is gratefully acknowledged. The National Science Foundation provided a portion of the funds for the purchase of the X-ray (Grant CHE-7820347) and NMR (Grant PCM-8115599) equipment. We are grateful to Professors R. Bergman and C. Kubiak for helpful discussions and for disclosing results prior to publication.

Supplementary Material Available: ^{31}P NMR spectra of **2** and **3**, tables of positional parameters for **1**, **2**, and **4**, thermal parameters for **1**, **2**, and **4**, torsion angles for **1**, **2**, and **4**, dppm bond distances and angles for **1**, **2**, and **4**, and least-squares planes for **1** and **2** (23 pages); a listing of structure factors for **1**, **2**, and **4**, (48 pages). Ordering information is given on any current masthead page.

Template Synthesis of the Macrobicyclic Ligand 1,5,8,12,15-Pentaazabicyclo[10.5.2]nonadecane: Evidence for Imidate and Enamine Intermediates Stabilized by Copper(II)

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Abstract: The pentadentate macrobicyclic ligand 1,5,8,12,15-pentaazabicyclo[10.5.2]nonadecane (L3), in which 1,4,7-triazacyclononane and cyclam (1,4,8,11-tetraazacyclotetradecane) are "fused", has been synthesized. The reactions involve condensation of [*N*,*N*′-bis(aminopropyl)-1,4,7-triazacyclononane]copper(II), $[Cu(L)]^{2+}$, with glyoxal followed by reduction and demetalation. This process represents one of the few successful ring-closure condensations of this type at a copper center. A detailed mechanism, involving two unusual intermediates that have been isolated and characterized, is provided. The condensation results in the formation of the imidate complex $[Cu(L1)]^{2+}$ via MeOH addition across a C=N bond. This imidate is unusual in that it is extremely resistant to acid hydrolysis, but it does undergo base hydrolysis to yield the first example of an amide formed by the condensation of a diamine with glyoxal. Incomplete reduction of the imidate (BH_4^-) affords a complexed enamine cation, $[Cu(L2)]^{2+}$. The perchlorate salt of $[Cu(L1)]^{2+}$ crystallized in the monoclinic space group $P2_1/c$ (a = 8.492 (2), b = 17.240 (6), c = 15.696 (4) Å; β = 96.47 (2)°). Refinement converged at R = 0.0855 for 286 parameters with 1626 reflections with $I > 3\sigma(I)$. The complex is square-pyramidal and contains an imidate group (C=N = 1.28 (2) Å). One of the perchlorate anions was disordered along the C_3 axis, with occupancy factors of 0.45 and 0.55 for the two resolved configurations. The perchlorate salt of $[Cu(L2)]^{2+}$ crystallized in the orthorhombic space group $Pbca$ (a = 14.144 (5), b = 16.815 (6), c = 18.236 (5) Å). Refinement converged at R = 0.0619 for 283 parameters with 2658 reflections with $I > 2\sigma(I)$. The complex is square-pyramidal with an enamine group showing a very short carbon–carbon double bond (1.213 (14) Å).

Remarkable differences in reactivity are frequently noted on the coordination of an organic moiety to a metal center. This is especially true for imines,[1] which, when unbound, are generally very readily hydrolyzed. However, when incorporated into a macrocyclic metal (e.g., nickel(II)) complex, species containing such functional groups may be recrystallized from acidic (1 M) solutions.[2] These observations have led to the use of metal amine complexes as templates in reactions with dialdehydes in the formation of macrocycles.[3,4] Barefield[5] has shown that a variety of N-alkylated amines, when complexed to nickel(II), condense with glyoxal to yield stable diimines, which may then be further reduced to derivatives of cyclam (1,4,8,11-tetraazacyclotetradecane). Notably in the latter step, although Ni(II) species reacted to give good yields, the corresponding copper ions exhibited re-

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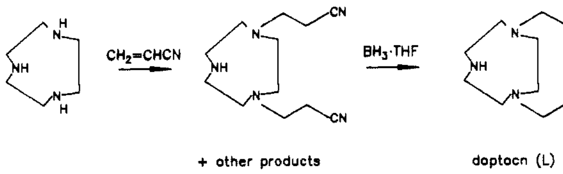
Scheme I. Synthetic Route to daptacn



duction at the metal center, precipitating Cu(0). Recently,[6] in our laboratory we have demonstrated the first successful condensation of a functionalized cyclam promoted by copper(II) where a fifth coordination site was available for binding to the metal center.

The latter reaction (coordinated imine–amine reduction) achieved usually with BH_4^- has been the subject of continued speculation as to the mechanism. Such discussion arises from the considerable instability of (especially uncomplexed) imidates (imino ethers), which could be formed as intermediates. Imidates are receiving increasing attention from both synthetic and mechanistic points of view. These centers have been shown to be reactive toward electrophiles and nucleophiles at the imino nitrogen and imino carbon centers, respectively. Among novel strategies for their formation presented recently are nitrogen-hydride insertion[7] into the metal–carbene bond of Fisher-type carbene complexes, enhanced silyl group exchange between N and O via chelation to nickel[8] (disilylamide to -imidate tautomerism), and derivation[9] from μ_3-NPh ligands of $Fe_3(\mu\text{-NPh})_2(CO)_9$.

In this paper we describe details of the mechanism of reduction, in aqueous methanol, of imine to amine, together with the characterization of a dicarbinolamine and an imine–carbinolamine as intermediates. Intervention of methanol in a nucleophilic addition to the monoimine produces an imidate complex. Base hydrolysis of the imidate moiety leads to the first example of the synthesis of an amide from the condensation reaction between a diimine and glyoxal.

Experimental Section

All materials were of reagent grade, except where otherwise indicated. Infrared spectra were obtained as KBr disks with a Perkin-Elmer 283 grating spectrometer. High-field ^1H and ^{13}C spectra were obtained with a Bruker WM 250 instrument. All chemical shifts are reported relative to tetramethylsilane (TMS).

UV-visible spectra were run on either a Cary 17 or a Perkin-Elmer Lambda 4B dual-beam spectrophotometer.

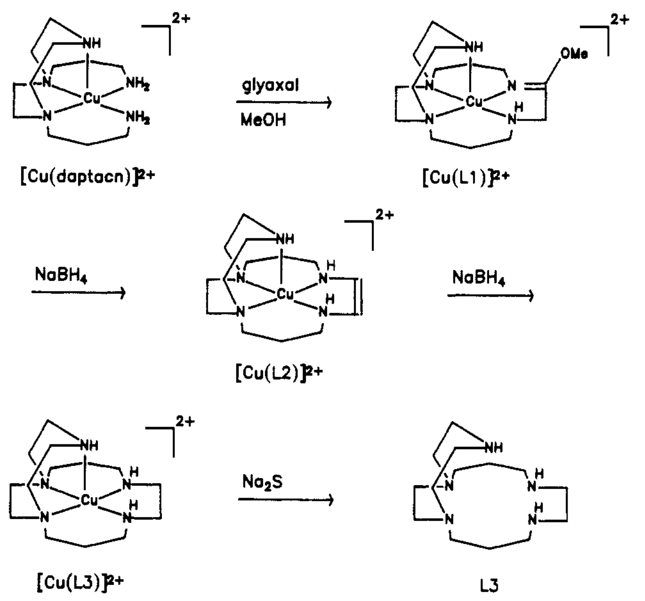
Elemental analyses were performed by Canadian Microanalytical Services, Vancouver, BC, Canada.

Synthesis

The complex ion used to effect macrocycle condensation was $[Cu(daptacn)]^{2+}$ (L = daptacn = *N,N'*-(diaminopropyl)-1,4,7-triazacyclononane). The daptacn ligand has been prepared in our laboratories[10] through the Michael addition of acrylonitrile to 1,4,7-triazacyclononane (2:1 stoichiometry); see Scheme I.

Following reduction of the mixture of acrylonitrile adducts, the various pendant arm macrocycles were isolated (Sephadex C50 column) as the corresponding nickel(II) complexes. Reaction with 6 M HCl followed by separation of the metal ion with Dowex ion-exchange chromatography yielded the protonated ligand $[H_5L]Cl_5 \cdot 2H_2O$. Both $Ni(L)^{2+}$ and $Cu(L)^{2+}$ complexes have been characterized.[10] Initially, condensation with glyoxal to produce the ring-closed fused macrobicyclic ligand was attempted with the nickel complex, in view of the better results obtained with Ni(II) as a template for cyclam formation. However, on reaction, a brown polymeric solid was formed that resisted characterization. However, by use of the corresponding $[CuL^{2+}]$ ion, shown by X-ray studies to be five-coordinate,[10] a smooth reaction with glyoxal was carried out in methanol/water mixtures. The synthetic route to the bicyclo N_5 ligand (L3) is presented in Scheme II.

Scheme II. Synthetic Route to L3



$Cu(daptacn)(ClO_4)_2$ [[Cu(L)]$(ClO_4)_2$]. Daptacn·$5HCl \cdot 2H_2O$ (2.05 g, 4.44 mmol) was added to a solution of NaOH (1.03 g, 24.1 mmol) in water (20 mL). After dilution to 100 mL with ethanol, the mixture was heated to 60 °C before a solution of $Cu(H_2O)_6(ClO_4)_2$ (1.53 g, 4.81 mmol in 10 mL of 50% ethanol) was added. The reaction mixture instantaneously turned dark blue, but stirring at 60 °C was continued for 20 min. The volume was reduced to 25 mL under reduced pressure, and the resulting precipitate was filtered off, rinsed with cold H_2O and then ethanol, and air-dried. A second crop was obtained after the volume was reduced further (to 5 mL) and the solution allowed to stand overnight. Total yield: 1.79 g (3.53 mmol, 80%). Anal. Calcd for $[Cu(C_{12}H_{29}N_5)](ClO_4)_2$: C, 28.49; H, 5.77; N, 13.84; Cl, 14.01. Found: C, 28.28; H, 5.77; N, 13.59; Cl, 13.49.

(6-Methoxy-1,5,8,12,15-pentaazabicyclo[10.5.2]nonadec-5-ene)copper Diperchlorate [[Cu(L1)]$(ClO_4)_2$]. To a solution of Cu(daptacn)$(ClO_4)_2$ (1.23 g, 2.4 mmol) in a mixture of water (60 mL) and methanol (1200 mL) was added glyoxal (450 μL of a 40% solution, 3.1 mmol). The solution was refluxed overnight, and then the volume was reduced to 60 mL under reduced pressure. Upon standing, a precipitate formed, which was filtered off, rinsed with methanol, and air-dried. Upon further reduction of the volume to 15 mL, a second crop of crystals was obtained. Total yield: 1.11 g, (1.97 mmol, 82%). Anal. Calcd for $[Cu(C_{15}H_{31}N_5O)](ClO_4)_2$: C, 32.20; H, 5.59; N, 12.52; Cl, 12.69; O, 25.76. Found: C, 32.29; H, 5.57; N, 12.52; Cl, 12.53; O, 24.34. IR: NH stretches, 3410, 3355; C=N stretch, 1650 cm^{-1}.

(1,5,8,12,15-Pentaazabicyclo[10.5.2]nonadec-6-ene)copper Diperchlorate [[Cu(L2)]$(ClO_4)_2$]. When a solution of [Cu(L1)]$(ClO_4)_2$ in a methanol/water solvent mixture (9:1) was reacted with slightly less than 2 mol equiv of $NaBH_4$ and treated in a manner similar to that for compound [Cu(L3)]$(ClO_4)_2$, a purplish blue powder was obtained. Upon recrystallization from hot water, a few crystals grew overnight that were suitable for X-ray analysis.

(1,5,8,12,15-Pentaazabicyclo[10.5.2]nonadecane)copper Diperchlorate [Cu(L3)$(ClO_4)_2$]. To a solution of [Cu(L1)]$(ClO_4)_2$ (825 mg, 1.47 mmol) in a methanol/water solvent mixture (9:1, 800 mL) was added $NaBH_4$ (130 mg, 3.4 mmol, 2.3 mol equiv), over a 10-min period. The solution was then refluxed for 60 min, cooled to room temperature, taken to dryness under reduced pressure, and then suspended in methanol (50 mL). The precipitate was filtered off, rinsed with methanol, and air-dried. Yield: 630 mg (1.19 mmol, 80%). Anal. Calcd for $[Cu(C_{14}H_{31}N_5)](ClO_4)_2$: C, 31.61; H. 5.87; N, 13.16; Cl, 13.33; O, 24.06. Found: C, 31.79; H, 5.89; N, 13.20; Cl, 13.21; O, 23.10. IR: NH stretches, 3420, 3380, 3360, 3320 cm^{-1}.

1,5,8,12,15-Pentaazabicyclo[10.5.2]nonadecane Tetrahydrochloride [L3·4HCl]. After the [Cu(L3)]$(ClO_4)_2$ complex (500 mg, 0.94 mmol) was dissolved in water (250 mL) and excess Na_2S (5–10 g) added, the solution was refluxed overnight. The resulting solution was colorless apart from a black precipitate of CuS.

Following filtration of the cooled mixture through a fine glass frit, the supernatant was taken to dryness. The residue was extracted into CH_2Cl_2 (3 × 50 mL) from 3 M NaOH (30 mL). The organic fractions were combined and dried over Na_2SO_4, and the solvent was removed, yielding

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Table I. Crystallographic Data

	$[Cu(L1)](ClO_4)_2$	$[Cu(L2)](ClO_4)_2$
formula	$CuCl_2O_9N_5C_{15}H_{31}$	$CuCl_2O_8N_5C_{14}H_{29}$
MW	559.9	529.86
space group	$P2_1/c$	*Pbca*
cell dimens		
a, Å	8.492 (2)	14.144 (5)
b, Å	17.240 (6)	16.815 (6)
c, Å	15.696 (4)	18.236 (5)
β, deg	96.47 (2)	90.0
V, Å^3	2283.3	4337.1
Z	4	8
D_c, g/cm^3	1.625	1.623
D_m, g/cm^3	1.611	1.604
T, °C	20 ± 2	20 ± 2
λ, Å	0.71069	0.71069
μ, cm^{-1}	12.73	13.24
transmissn coeff	0.608–0.846	0.607–0.695
$R(F_o)$	0.0855	0.0619
R_w	0.1049	0.0807

the free ligand as a colorless hydroscopic oil. MS (CI): 270 (M + 1), 298 (M + 29), 310 (M + 41). ^{13}C NMR ($CDCl_2$): δ 26.0 (CCH_2C), 45.1, 46.6, 47.3, 52.7, 53.1, 54.4 (CH_2N).

The ligand was stored as the hydrochloride salt: The oil was dissolved in DMF (15 mL), and concentrated HCl was added (3 mL). After the mixture was taken to dryness, the residue was suspended in warm DMF (10 mL) and then cooled. The white powdery precipitate was filtered off, rinsed with cold ethanol, and air-dried. Yield: 318 mg (0.77 mmol, 82%). Anal. Calcd for $C_{14}H_{35}N_5Cl_4$: C, 40.49; H, 8.49; N, 16.86; Cl, 34.14. Found: C, 39.39; H, 8.50; N, 16.24; Cl, 34.42. ^{13}C NMR (D_2O): δ 20.7 (CCH_2C), 38.1, 40.8, 42.0, 47.9, 49.6, 52.0 (CH_2N).

(6-Oxo-1,5,8,12,15-pentaazabicyclo[10.5.2]-5-nonadecyl)copper Perchlorate (8). The copper complex $[Cu(L1)](ClO_4)_2$ (25 mg, 0.045 mmol) was dissolved in methanol (5 mL) containing a trace of NaOMe. The solution was refluxed 3 h, then acidified with $HClO_4$, and taken to dryness. The residue was recrystallized from layering of an aqueous solution (1 mL) with isopropyl alcohol (3–4 mL). Yield: 10 mg, (0.022 mmol, 50%). IR: NH stretches, 3150 cm^{-1} (br); C=O stretch, 1577 cm^{-1}.

6-Oxo-1,5,8,12,15-pentaazabicyclo[10.5.2]nonadecane (10). To a solution of the copper complex $[Cu(L1)](ClO_4)$ (75 mg, 0.13 mmol) in water (2 mL) was added a solution of Na_2S (3 mL of a 0.12 M, 0.36 mmol). The pH of this solution was ≈13, so that oxo complex **7** was produced in situ. After the solution was refluxed for 3 h, the CuS precipitate was filtered through a fine glass frit. The supernatant was saturated with sodium carbonate before extraction with CH_2Cl_2 (3 × 10 mL). The CH_2Cl_2 fractions were combined, dried over Na_2SO_4, and taken to dryness under reduced pressure, leaving a hydroscopic residue. Yield: 22 mg (0.078 mmol, 58%). ^{13}C NMR ($CDCl_3$): δ 24.7, 26.8 (CCH_2C), 41.2, 42.5, 46.0, 46.7, 47.3, 51.4, 51.7, 53.0, 54.2, 56.1 (CH_2N), 61.0 ($OCCH_2N$), 171.8 (CO). ^1H NMR ($CDCl_3$): δ 8.25 ($NHCO$), 2.2–3.9 (br m, CH_2N), 1.75 (m, $CH_2CH_2CH_2$). MS: 284 (M + 1), 312 (M + 29), 324 (M + 41).

Crystallography

The experimental parameters for both complexes are listed in Table I with additional information in Table S12 (supplementary material). Crystals were mounted in glass Lindemann tubes and the unit cells and space groups determined with the use of Weissenberg and precession photography, after which the crystals were transferred to a Picker four-circle diffractometer automated with a PDP 11/10 computer.

$[Cu(L1)](ClO_4)_2$. The unit cell was refined with 20 pairs of reflections in the 2θ range 13–39°. The intensity measurements were obtained by scanning in the $\theta/2\theta$ mode with 200 steps of 0.01° in 2θ, counting for 0.50 s/step. Background counting was introduced for 50 s at each end of the scan. A set of three standard reflections preceded each batch of 50 measurements, with no noticeable change in intensity observed during the collection.

For both crystal structures, solution of the phase problem was achieved by direct methods with SHELX76.[11] The atomic scattering factors were those included in the SHELX76 program together with the Cu f curve from ref 12. In the case of $[Cu(L1)](ClO_4)_2$, completion and refinement of the structure were carried out by difference electron density maps and least squares. All atoms were refined anisotropically except for oxygen O6, O7, O8 and O66, O77, O88, which were refined isotropically. These oxygens are part of two different orientations found for one of the perchlorate anions, which was disordered. The site occupancy factor for the first set (O6, O7, O8) is 0.45 while that of the other set is 0.55. The hydrogen atoms were not included in the calculations owing to the small number of observed reflections. The refinement converged with a maximum shift/esd of 0.021 on the final cycle and a maximum unassigned electron density of 0.56 e Å^{-3} on the final difference map. The final R value is 0.0855, and R_w = 0.1049.

$[Cu(L2)](ClO_4)_2$. The unit cell was refined with the use of 18 pairs of reflections in 2θ from 17 to 47°. The intensity measurements were obtained by scanning in the $\theta/2\theta$ mode with 200 steps of 0.01° in 2θ, counting for 0.25 s/step. Background counting was introduced for 25 s at each end of the scan. A set of three standard reflections preceded each batch of 50 measurements, with no detectable change in intensity observed during the collection. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms on the nitrogens were observed and refined isotropically. Most, but not all, of the other hydrogen atoms were also observed. For the sake of uniformity, all of the carbon hydrogen atoms were placed at calculated positions (C–H = 1.08 Å). The solution converged with a maximum shift/esd of 0.03 in the last cycle and a maximum unassigned electron density peak of 1.0 e Å^{-3}. The final R value is 0.0629, and R_w = 0.0807.

Results and Discussion

The macrocyclic ligand L3 was synthesized according to the reaction sequence reported recently for the analogous SN_4 macrocyclic ligand 15-thia-1,5,8,12-tetraazabicyclo[10.5.2]nonadecane,[6] i.e., through the Schiff-base condensation of a diamine with glyoxal, followed by reduction of the intermediate by borohydride. However, in the present system we have successfully isolated and structurally characterized the species $[Cu(L1)]^{2+}$ and $[Cu(L2)]^{2+}$.

Whereas in most instances the primary product characterized in the Schiff-base condensation has been shown to be the diimine, there is evidence for imine–carbinolamine intermediates. In principle, the condensation of a carbonyl compound with a diamine can give rise to three different products depending on the degree of dehydration that occurs. These are (a) dicarbinolamine, (b) imine–carbinolamine, and (c) diimine. A crystal structure of a dicarbinolamine has been presented by Tasker et al.[13] Condensation of 2,6-diformylpyridine with dihydrazinopyridine results in an intermediate diol that permits folding of the macrocycle, thus releasing the ring from an otherwise planar five-coordinate arrangement. Similar steric arguments have been advanced in the case of planar N_4 systems,[14] which have also been identified. Hydrated material produced from a nickel(II) amine/glyoxal reaction, which was difficult to characterize, gave infrared data consistent with an imine–carbinolamine complex. Also, attack of methoxide or ethoxide on two imine functions in a N_4 macrocycle[15] yields a bis(α-amino ether) derivative. A similar addition of alcohol across one imine function has been reported[16] in a Schiff-base complex coordinated to copper(II).

Two reactions of interest have been identified in the present paper. Whereas there is compelling evidence for formation of an imine–carbinolamine intermediate, the surprising result is that the complex isolated is an imidate $[Cu(L1)]^{2+}$. Also, partial reduction of this species with BH_4^- results in the enamine $[Cu(L2)]^{2+}$. Similar data have been observed in our laboratories[17] for the ligand based on the macrobicycle N_4O, where the apical donor is an oxygen atom. Further reduction with borohydride provides the fully reduced macrocyclic ion $[Cu(L3)]^{2+}$.

Molecular Structures

The structures of $[Cu(L1)^{2+}]$ and $[Cu(L2)^{2+}]$ are shown in Figures 1 and 2. Five-coordinate geometry of the Cu(II) ion is maintained in both systems.

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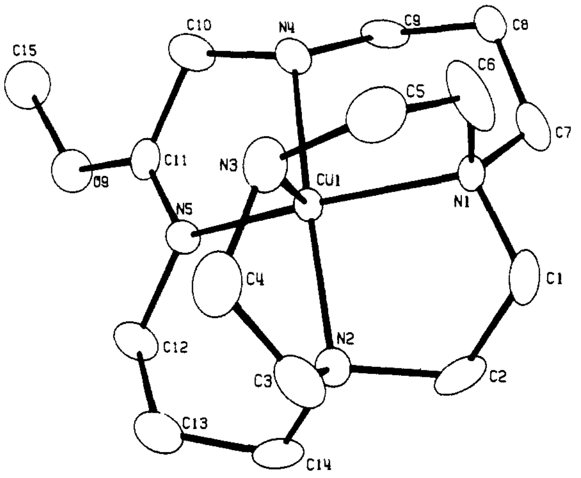

Figure 1. ORTEP diagram for $[Cu(L1)]^{2+}$, showing 20% ellipsoids.

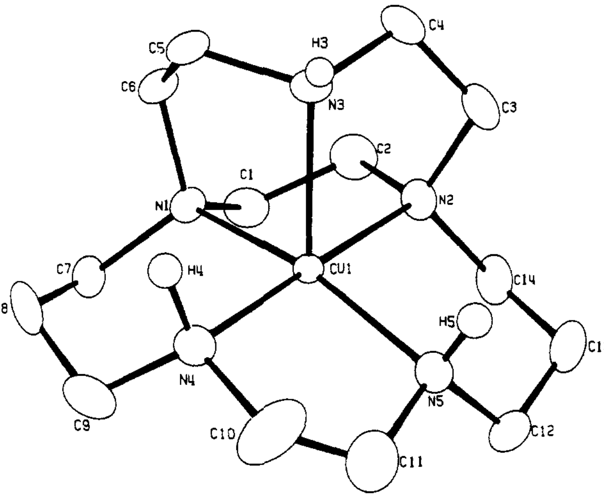

Figure 2. ORTEP diagram for $[Cu(L2)]^{2+}$, showing 20% thermal ellipsoids. For clarity only the amine hydrogens are shown.

$[Cu(L1)]^{2+}$. X-ray-quality crystals of the perchlorate salt were obtained from a solvent mixture of acetonitrile/ether. The bond lengths are listed in Table II and the bond angles in Table III. The crystal structure consists of the complex cation packed with two perchlorate counterions. The coordination geometry at the copper center is square-pyramidal and very similar[10] to that for $[Cu(daptacn)]^{2+}$, apart from the presence of an additional chelate ring, to which attention is now directed. The N5–C11 distance (1.28 (2) Å) is particularly short for a N–C bond and must correspond to a double bond. In fact, the distance observed is in good agreement with the predicted theoretical value[18] of 1.282 Å for an imidate N═C bond. (Of interest is a recent finding in our laboratory[17] of a conjugated diimine derived from Ni(II) cyclam. In this complex, the C–N bond lengths (1.29, 1.30 Å) reflect the multiple-bond character of such systems.) The double-bond nature of the N5–C11 bond is also reflected in the bond angles at C11 and N5. At C11, the three bond angles are all 120° within experimental error, whereas at N5 the C11–N5–Cu angle is smaller than expected (114 (1)°) while the C11–N5–C12 angle is larger (127 (1)°), reflecting the "pull" exerted by C10 to allow the formation of the five-membered chelate ring; the sum of the bond angles at each center is 360°, indicating planarity. This is confirmed by mean plane calculations involving the atoms O9, C11, C10, N5, C12, and Cu (see Table S8 (supplementary material)).

The C11–O9 distance of 1.34 (2) Å is considerably shorter than the C15–O9 distance (1.48 (2) Å), consistent with the predicted π-bond character of the former due to the contribution of the resonance structure B. The resonance contribution of structure

B is also reflected by the fact that C15 is only slightly (0.06 (2)

Table II. Interatomic Distances (Å) for $[Cu(L1)](ClO_4)_2$

atoms	distance[a]	atoms	distance[a]
N(1)–Cu(1)	2.093 (12)	C(11)–O(9)	1.35 (2)
N(2)–Cu(1)	2.062 (15)	C(15)–O(9)	1.48 (2)
N(3)–Cu(1)	2.205 (14)	C(1)–N(1)	1.42 (2)
N(4)–Cu(1)	2.043 (13)	C(6)–N(1)	1.50 (2)
N(5)–Cu(1)	1.963 (12)	C(7)–N(1)	1.51 (2)
O(1)–Cl(1)	1.416 (13)	C(2)–N(2)	1.56 (2)
O(2)–Cl(1)	1.366 (16)	C(3)–N(2)	1.44 (2)
O(3)–Cl(1)	1.410 (14)	C(14)–N(2)	1.55 (2)
O(4)–Cl(1)	1.307 (15)	C(4)–N(3)	1.50 (2)
O(5)–Cl(2)	1.425 (14)	C(5)–N(3)	1.49 (2)
O(6)–Cl(2)	1.37 (4)	C(9)–N(4)	1.46 (2)
O(7)–Cl(2)	1.40 (4)	C(10)–N(4)	1.49 (2)
O(8)–Cl(2)	1.46 (3)	C(11)–N(5)	1.28 (2)
O(66)–Cl(2)	1.60 (5)	C(12)–N(5)	1.49 (2)
O(77)–Cl(2)	1.46 (3)	C(2)–C(1)	1.46 (2)
O(88)–Cl(2)	1.39 (3)	C(4)–C(3)	1.56 (3)
O(66)···O(6)	1.27 (5)	C(6)–C(5)	1.44 (3)
O(77)···O(6)	1.12 (4)	C(8)–C(7)	1.49 (3)
O(77)···O(7)	1.62 (5)	C(9)–C(8)	1.55 (3)
O(88)···O(7)	1.05 (4)	C(11)–C(10)	1.50 (2)
O(66)···O(8)	1.37 (5)	C(13)–C(12)	1.49 (3)
O(88)···O(8)	1.66 (5)	C(14)–C(13)	1.57 (3)

[a] Estimated standard deviations are given in parentheses.

Table III. Bond Angles (deg) for $[Cu(L1)](ClO_4)_2$

atoms	angle[a]	atoms	angle[a]
N(2)–Cu(1)–N(1)	84.5 (6)	C(1)–N(1)–Cu(1)	107.7 (11)
N(3)–Cu(1)–N(1)	82.3 (6)	C(6)–N(1)–Cu(1)	106.6 (12)
N(3)–Cu(1)–N(2)	84.3 (6)	C(6)–N(1)–C(1)	110.9 (17)
N(4)–Cu(1)–N(1)	92.9 (6)	C(7)–N(1)–Cu(1)	111.6 (10)
N(4)–Cu(1)–N(2)	174.4 (6)	C(7)–N(1)–C(1)	110.5 (14)
N(4)–Cu(1)–N(3)	100.3 (6)	C(7)–N(1)–C(6)	119.6 (15)
N(5)–Cu(1)–N(1)	162.4 (6)	C(2)–N(2)–Cu(1)	101.0 (11)
N(5)–Cu(1)–N(2)	97.0 (6)	C(3)–N(2)–Cu(1)	110.4 (12)
N(5)–Cu(1)–N(3)	115.3 (6)	C(3)–N(2)–C(2)	112.9 (17)
N(5)–Cu(1)–N(4)	83.9 (6)	C(14)–N(2)–Cu(1)	115.1 (12)
O(2)–Cl(1)–O(1)	112.2 (10)	C(14)–N(2)–C(2)	101.1 (15)
O(3)–Cl(1)–O(1)	111.3 (9)	C(14)–N(2)–C(3)	115.1 (16)
O(3)–Cl(1)–O(2)	105.3 (11)	C(4)–N(3)–Cu(1)	98.9 (12)
O(4)–Cl(1)–O(1)	110.6 (11)	C(5)–N(3)–Cu(1)	107.1 (13)
O(4)–Cl(1)–O(2)	106.2 (14)	C(5)–N(3)–C(4)	120.3 (18)
O(4)–Cl(1)–O(3)	110.9 (14)	C(9)–N(4)–Cu(1)	114.0 (10)
O(6)–Cl(2)–O(5)	108 (2)	C(10)–N(4)–Cu(1)	109.3 (10)
O(7)–Cl(2)–O(5)	111 (2)	C(10)–N(4)–C(9)	110.8 (15)
O(7)–Cl(2)–O(6)	114 (2)	C(11)–N(5)–Cu(1)	114.5 (12)
O(8)–Cl(2)–O(5)	108 (2)	C(12)–N(5)–Cu(1)	126.7 (11)
O(8)–Cl(2)–O(6)	102 (2)	C(12)–N(5)–C(11)	118.7 (14)
O(8)–Cl(2)–O(7)	114 (2)	C(2)–C(1)–N(1)	115 (2)
O(66)–Cl(2)–O(5)	114 (2)	C(1)–C(2)–N(2)	108 (2)
O(66)–Cl(2)–O(6)	50 (2)	C(4)–C(3)–N(2)	112 (2)
O(66)–Cl(2)–O(7)	135 (2)	C(3)–C(4)–N(3)	110 (2)
O(66)–Cl(2)–O(8)	53 (2)	C(6)–C(5)–N(3)	116 (2)
O(77)–Cl(2)–O(5)	114 (1)	C(5)–C(6)–N(1)	114 (2)
O(77)–Cl(2)–O(6)	47 (2)	C(8)–C(7)–N(1)	117 (2)
O(77)–Cl(2)–O(7)	69 (2)	C(9)–C(8)–C(7)	117 (2)
O(77)–Cl(2)–O(8)	134 (2)	C(8)–C(9)–N(4)	113 (2)
O(77)–Cl(2)–O(66)	91 (2)	C(11)–C(10)–N(4)	109 (1)
O(88)–Cl(2)–O(5)	115 (2)	N(5)–C(11)–O(9)	119 (2)
O(88)–Cl(2)–O(6)	137 (2)	C(10)–C(11)–O(9)	121 (2)
O(88)–Cl(2)–O(7)	44 (2)	C(10)–C(11)–N(5)	121 (2)
O(88)–Cl(2)–O(8)	71 (2)	C(13)–C(12)–N(5)	113 (2)
O(88)–Cl(2)–O(66)	114 (2)	C(14)–C(13)–C(12)	115 (2)
O(88)–Cl(2)–O(77)	107 (2)	C(13)–C(14)–N(2)	106 (2)
C(15)–O(9)–C(11)	119 (4)		

[a] Estimated standard deviations are given in parentheses.

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(18) Hafelinger, G. In *The Chemistry of Amidines and Imidates*; Patai, S., Ed.; Wiley, Interscience: New York, 1975; pp 1–84.

Table IV. Interatomic Distances (Å) for $[Cu(L2)](ClO_4)_2$

atoms	distance[a]	atoms	distance[a]
N(1)-Cu(1)	2.053 (5)	C(3)-N(2)	1.513 (11)
N(2)-Cu(1)	2.067 (5)	C(14)-N(2)	1.477 (10)
N(3)-Cu(1)	2.206 (6)	C(4)-N(3)	1.485 (10)
N(4)-Cu(1)	2.017 (5)	C(5)-N(3)	1.487 (10)
N(5)-Cu(1)	2.027 (6)	C(9)-N(4)	1.453 (13)
O(1)-Cl(1)	1.465 (11)	C(10)-N(4)	1.510 (14)
O(2)-Cl(1)	1.305 (8)	C(11)-N(5)	1.489 (11)
O(3)-Cl(1)	1.413 (9)	C(12)-N(5)	1.478 (11)
O(4)-Cl(1)	1.371 (8)	C(2)-C(1)	1.500 (11)
O(5)-Cl(2)	1.418 (6)	C(4)-C(3)	1.438 (12)
O(6)-Cl(2)	1.427 (6)	C(6)-C(5)	1.497 (11)
O(7)-Cl(2)	1.383 (6)	C(8)-C(7)	1.490 (14)
O(8)-Cl(2)	1.412 (5)	C(9)-C(8)	1.540 (16)
C(1)-N(1)	1.496 (9)	C(11)-C(10)	1.213 (14)
C(6)-N(1)	1.508 (9)	C(13)-C(12)	1.493 (13)
C(7)-N(1)	1.508 (9)	C(14)-C(13)	1.511 (13)
C(2)-N(2)	1.484 (9)		

[a] Estimated standard deviations are given in parentheses.

Table V. Bond Angles (deg) for $[Cu(L2)](ClO_4)_2$

atoms	angle[a]	atoms	angle[a]
N(2)-Cu(1)-N(1)	86.1 (2)	C(3)-N(2)-Cu(1)	102.4 (5)
N(3)-Cu(1)-N(1)	84.1 (2)	C(3)-N(2)-C(2)	113.1 (6)
N(3)-Cu(1)-N(2)	82.5 (3)	C(14)-N(2)-Cu(1)	114.0 (5)
N(4)-Cu(1)-N(1)	96.0 (3)	C(14)-N(2)-C(2)	107.1 (7)
N(4)-Cu(1)-N(2)	177.8 (2)	C(14)-N(2)-C(3)	112.4 (6)
N(4)-Cu(1)-N(3)	98.3 (3)	C(4)-N(3)-Cu(1)	106.8 (5)
N(5)-Cu(1)-N(1)	165.1 (3)	C(5)-N(3)-Cu(1)	102.0 (4)
N(5)-Cu(1)-N(2)	92.9 (2)	C(5)-N(3)-C(4)	116.1 (6)
N(5)-Cu(1)-N(3)	110.6 (3)	C(9)-N(4)-Cu(1)	118.4 (5)
N(5)-Cu(1)-N(4)	84.9 (3)	C(10)-N(4)-Cu(1)	105.8 (6)
O(2)-Cl(1)-O(1)	103.1 (8)	C(10)-N(4)-C(9)	115.3 (9)
O(3)-Cl(1)-O(1)	91.7 (7)	C(11)-N(5)-Cu(1)	106.3 (5)
O(3)-Cl(1)-O(2)	113.0 (6)	C(12)-N(5)-Cu(1)	116.8 (5)
O(4)-Cl(1)-O(1)	91.2 (7)	C(12)-N(5)-C(11)	111.9 (9)
O(4)-Cl(1)-O(2)	117.8 (6)	C(2)-C(1)-N(1)	110.8 (6)
O(4)-Cl(1)-O(3)	126.9 (7)	C(1)-C(2)-N(2)	111.1 (6)
O(6)-Cl(2)-O(5)	108.7 (4)	C(4)-C(3)-N(2)	112.7 (6)
O(7)-Cl(2)-O(5)	109.1 (5)	C(3)-C(4)-N(3)	111.1 (6)
O(7)-Cl(2)-O(6)	110.6 (5)	C(6)-C(5)-N(3)	110.9 (6)
O(8)-Cl(2)-O(5)	109.9 (4)	C(5)-C(6)-N(1)	114.1 (6)
O(8)-Cl(2)-O(6)	107.6 (4)	C(8)-C(7)-N(1)	114.0 (6)
O(8)-Cl(2)-O(7)	111.0 (5)	C(9)-C(8)-C(7)	115.0 (7)
C(1)-N(1)-Cu(1)	102.1 (4)	C(8)-C(9)-N(4)	111.4 (7)
C(6)-N(1)-Cu(1)	109.4 (4)	C(11)-C(10)-N(4)	119.2 (9)
C(6)-N(1)-C(1)	110.8 (6)	C(10)-C(11)-N(5)	117.8 (10)
C(7)-N(1)-Cu(1)	114.2 (4)	C(13)-C(12)-N(5)	111.2 (7)
C(7)-N(1)-C(1)	108.1 (6)	C(14)-C(13)-C(12)	116.3 (7)
C(7)-N(1)-C(6)	111.8 (5)	C(13)-C(14)-N(2)	115.2 (7)
C(2)-N(2)-Cu(1)	107.7 (4)		

[a] Estimated standard deviations are given in parentheses.

Å) out of the plane defined by O9—C11(C10)=N5(C12)—Cu.

The Cu-N5 bond (1.96 (1) Å) is the shortest of the bonds at the copper center. It is well documented[19] that, for the M(II) transition-metal ions, the M-N distances for all the macrocycles increase in the order pyridine < imine < amine. The remaining Cu-N distances are similar to those found for similar complexes; i.e., Cu-N4 (2.04 (1) Å) (a secondary nitrogen) is shorter than the Cu-N (tertiary) bonds in the plane, and the apical Cu-N3 bond (2.21 (1) Å) is the longest. The four equatorial nitrogens do not form an ideal plane (Table S8). The slight tetrahedral distortion from planarity of the N4 "plane" is probably a result of the rigidity of the imidate function. The incidence angle between the imidate plane and the N4 plane is 11.5°. The copper atom is positioned 0.21 (2) Å above the N4 plane toward the apical nitrogen. The angle between the N(ap)-Cu vector and the normal to the N4 plane is 17.5°. The degree of tugging on the apical nitrogen is greater[10] than for $[Cu(daptacn)]^{2+}$, a result of the increased displacement of the copper atom out of the N4 plane.

The perchlorate anions are held loosely together to the complex through weak hydrogen bonds. There are two close contacts between the secondary amines and oxygens from perchlorate where hydrogen bonding is possible. These are N4···O4 (2.994 Å) and N3···O5 (3.093 Å). Since the hydrogen atoms were not found, the angle at the hydrogens cannot be calculated.

One of the perchlorate anions was found to be disordered. The position of the chlorine and one of the oxygens (O5) was shared by both orientations; thus, the disorder was along the C_3 rotation axis. The two orientations refined with site occupancy factors of 0.45 and 0.55, respectively. No disorder of O5 was observed, as a result of its involvement in hydrogen bonding to N3.

$[Cu(L2)]^{2+}$. Crystals of the perchlorate salt were grown from a solution of the complex in CH_3CN in an ether atmosphere. The bond lengths are listed in Table IV and the bond angles in Table V. The structure consists of a five-coordinate copper complex and two perchlorate ions. The molecular structure of the complex cation is shown in Figure 2. Both perchlorate anions are held at fixed positions in the lattice through hydrogen bonding with the secondary amine protons in both cases, and one of the perchlorates is also held through a weak interaction (3.13 Å) with the vacant sixth coordination site at the copper center. Relevant intermolecular distances are listed in Table S13 (supplementary material). The weakly coordinated (through O3) perchlorate bridges another complex cation through a hydrogen bond involving N4-H4-O4. The other perchlorate is fixed through a pair of hydrogen bonds to the same complex cation (N3-H3-O8 and H5-H5-O6).

The coordination geometry at the copper center is best described as square-pyramidal, in spite of the weak interaction with oxygen O3 from one of the perchlorate. The bond lengths and angles at the copper center are remarkably similar to those observed[10] for $[Cu(daptacn)]^{2+}$, indicating that no undue strain was created by the formation of the 14-membered ring. The only anomalous value is the C10-C11 bond length (1.213 (14) Å), which is very short for a C-C double bond. However, the bond angles for N4-C10-C11 (119.2 (9)°) and C10-C11-N5 (117.8 (10)°) are typical for sp^2-hybridized carbon atoms. In the corresponding complex involving the ligand with an apical oxygen donor (N_4O), the C10-C11 bond is 1.34 Å in length[17] conforming to the C=C character. Noteworthy is the lengthening of this bond to 1.54 Å on reduction of the macrocyclic ring in the N_4O system.

As was the case for $[Cu(L1)]^{2+}$ there is a slight tetrahedral distortion of the four equatorial nitrogens. In the enamine, however, the copper atom is only 0.140 (1) Å out of the N_4 "plane" (Table S9 (supplementary material)), which is no greater than some of the nitrogen donors forming it. As was the case previously, there is some "tugging" on the apical nitrogen, the angle of incidence between the Cu-N3 vector and the N_4 plane being 14.5°.

It is of interest to note that whereas in $[Cu(cyclam)^{2+}]$[20] the stable trans-III configuration[21] of the macrocyclic ring is adopted, the trans-I form is observed in the $[Cu(L2)]^{2+}$ ion. Various studies[22,23] have shown the former geometry to have the lowest energy of the trans complexes. Of the other conformers possible for the macrobicycle, a molecular mechanics study by Connolly and Billo[23] shows the trans-I form to have the lowest relative strain energy for both planar and octahedral geometry at the metal center. Recent NMR evidence is consistent with the trans-I conformer having only slightly higher energy than the trans-III form.

Mechanistic Investigations

(a) Formation of the Imidate $[Cu(L1)]^{2+}$. The imidate intermediate isolated in the condensation reaction with glyoxal is not one of the three products anticipated for the reactions of this type. However, from Scheme III it may be seen that the imidate may be obtained from the imine–carbinolamine intermediate **2** through

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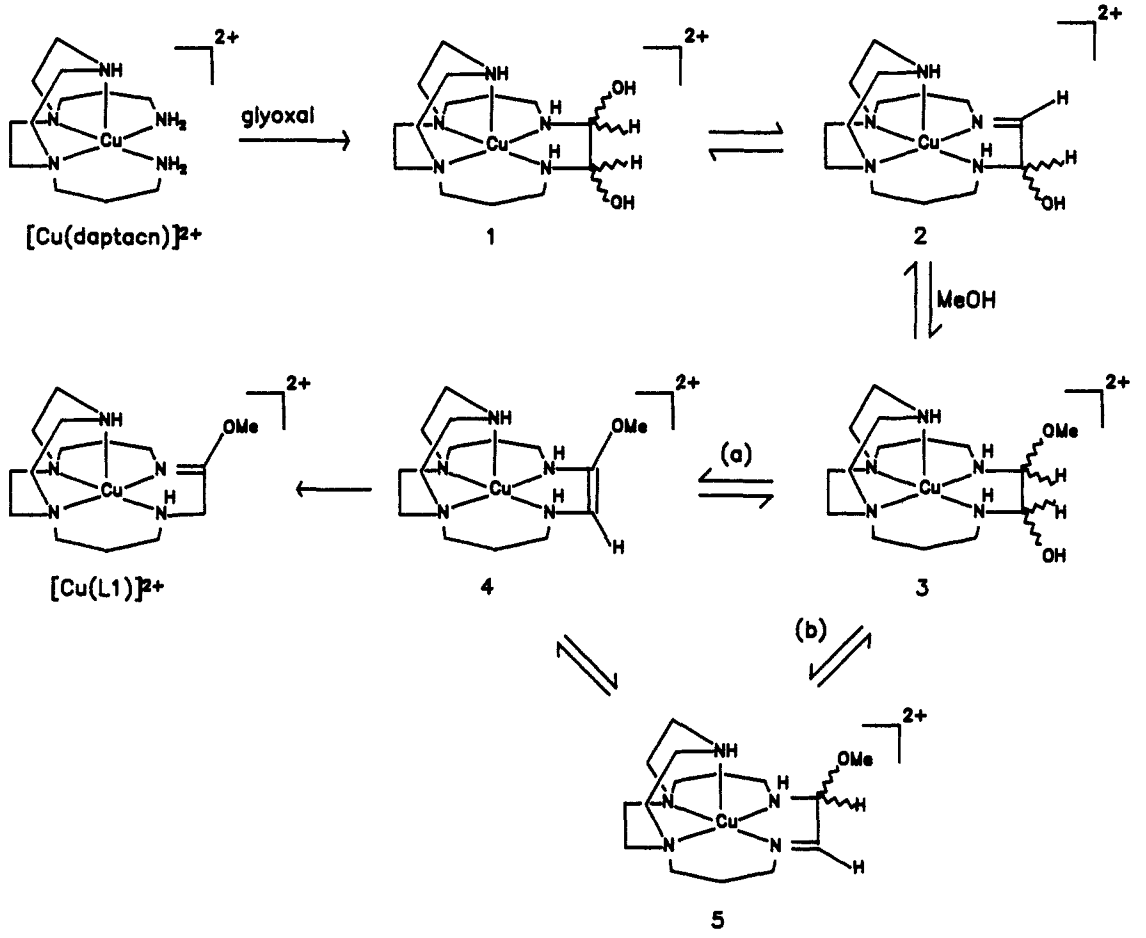
(20) Tasker, P. A.; Sklar, L. *J. Cryst. Mol. Struct.* **1975**, *5*, 329.

(21) Bosnich, B.; Poon, C. K.; Tobe, M. L. *Inorg. Chem.* **1965**, *4*, 1102.

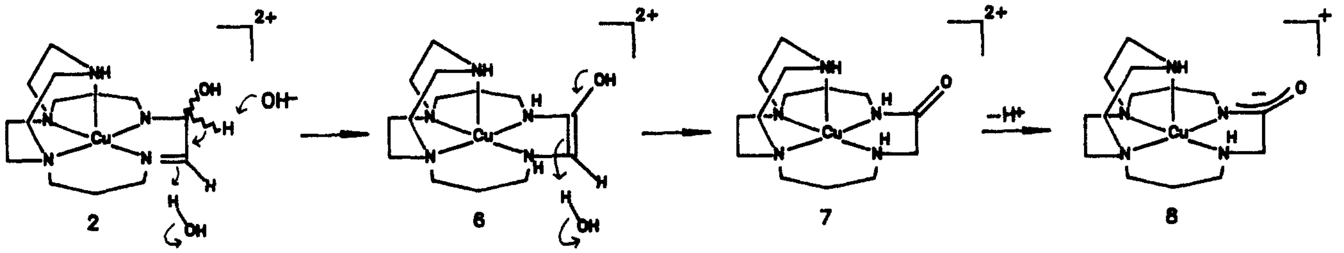
(22) Thom, V. J.; Fox, C. C.; Boeyens, J. A. C.; Hancock, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 5947.

(23) Connolly, P. J.; Billo, E. J. *Inorg. Chem.* **1987**, *26*, 553.

Scheme III. Proposed Mechanism for the Formation of $[Cu(L1)]^{2+}$ from the Reaction of $[Cu(daptacn)]^{2+}$ with Glyoxal



Scheme IV. Proposed Mechanism for the Base Hydrolysis of 2



a nucleophilic addition of methanol across the imine to give **3**, which can lose water to give **4** or **5**. Conversion to $[Cu(L1)]^{2+}$ involves simple enamine-imine prototropic shifts.

The condensation was carried out in various solvent mixtures. In water, or in a mixture of isopropyl alcohol/water, identical results were observed. The IR spectrum of the purple precipitate obtained showed a weak band at 1680 cm^{-1}, possibly due to a C=N stretch. Compared to the IR spectrum[10] of $[Cu(daptacn)]^{2+}$, the NH_2 scissor band at 1595 cm^{-1} and most of the NH stretches had disappeared, indicating that cyclization had occurred. This material was acid-stable, confirming cyclization. The material isolated from the condensation reaction of $[Cu(daptacn)]^{2+}$ with glyoxal in water or water/isopropyl alcohol mixtures is an equilibrium mixture of bis(carbinolamine) **1** and of imine-carbinolamine **2**. Treatment of this mixture with acid shifted the equilibrium toward **2**.

In their study of condensation reactions of linear tetraamines with glyoxal, Barefield et al.[5] have suggested that the product is an imine-carbinolamine complex, when the resulting macrocycle is a 14-membered ring, whereas a diimine complex was isolated for a 15-membered ring. These results also suggest the importance of steric factors. Apparently the 14-membered ring is too small to allow the formation of an α-diimine residue. The results of the present study support this hypothesis.

When the equilibrium mixture of **1** and **2** is treated with base, the product isolated exhibits a strong band appearing at 1575 cm^{-1} in the IR spectrum. The position of this band is typical for C=O stretch in coordinated amido complexes.[24] This is the first example of the synthesis of an amide from a condensation reaction between a diamine and glyoxal. Formation of the amide is thought to proceed via a base-catalyzed proton shift at the imine-carbinolamine intermediate **2**, generating enol **6**, which rapidly undergoes a tautomeric proton shift to give amide **7**. Deprotonation of **7** yields **8** (see Scheme IV). In support of this mechanism, ionization of methylene protons adjacent to an imine in a five-membered ring is well documented.[25]

In the addition of MeOH across the imine, reference has already been made[15,16] to additions of nucleophiles to coordinated imine functions.

The only remaining step to explain in the proposed mechanism is the dehydration of **3**. The pathway (a) involves dehydration across the C-C bond, although there is no evidence to rule out

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(24) Kushi, Y.; Achida, R.; Kimura, E. *J. Chem. Soc., Chem. Commun.* **1985**, 216.

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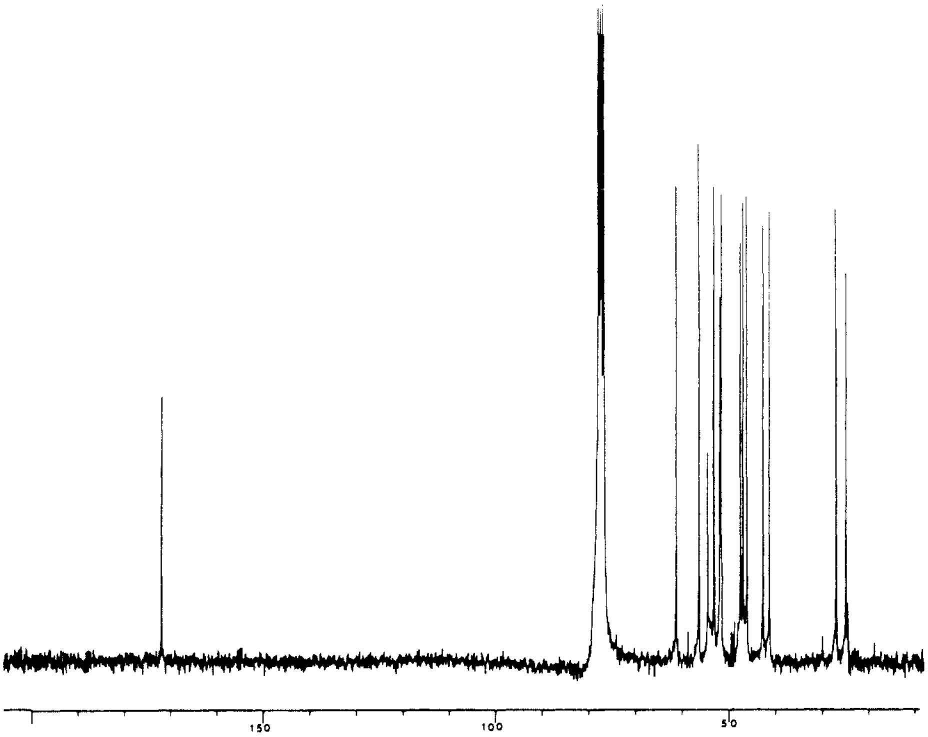
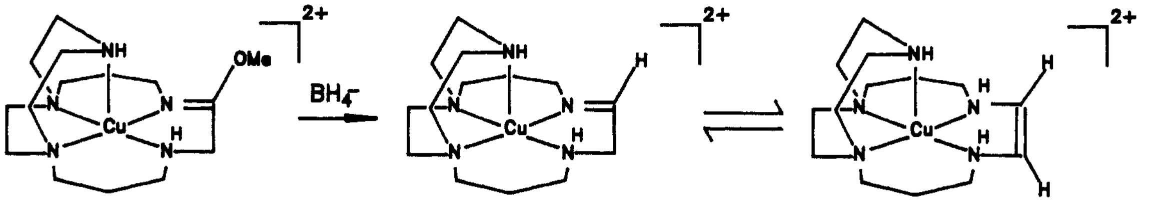


Figure 3. ^{13}C NMR spectrum of **10** in $CDCl_3$.

Scheme V. Proposed Mechanism for the Formation of the Enamine Complex $[Cu(L2)]^{2+}$



$[Cu(L1)]^{2+}$ **9** $[Cu(L2)]^{2+}$

a different route (b) in which dehydration occurs across the C–N bond to give imine **5**, which in turn undergoes a sequence of two proton shifts through imine–enamine tautomers.

Further mechanistic information was sought by deuterium-exchange experiments., The last step in the formation of the imidate function involves a proton shift from a nitrogen to a carbon center. Thus, if this step is reversible, deuterium atoms should be incorporated at that carbon center. When the complex $[Cu(L1)]^{2+}$ was refluxed in CH_3OD and then taken to dryness, N–H but no C–H exchange was observed. In CH_3OD containing 0.1 M $DClO_4$ and also in CH_3OD containing a trace of sodium methoxide, again only N–D stretches were observed. In the latter experiment, the C=N stretch at 1650 cm^{-1} disappeared and was replaced with a strong band at 1577 cm^{-1} (C=O stretch) corresponding to amide **8**.

From these deuterium-exchange experiments, it is evident that the conversion of **4** to $[Cu(L1)]^{2+}$ is an irreversible process. However, when the glyoxal condensation reaction was carried out in CH_3OD/D_2O, the IR spectrum of the product isolated from this reaction mixture contained not only the three N–D stretches already observed but also a broad C–D stretch, centered at 2340 cm^{-1}, indicating deuterium incorporation from the solvent at the methylene carbon.

(b) Reduction of the Imidate. The reduction[26] of N-substituted imidates with zinc or sodium amalgams in acid solution proceeds through initial reduction, giving an imine that hydrolyzes to give primary amines and aldehydes, whereas reduction with $NaBH_4$ generates secondary amines. A mechanism for the reduction of imidates with sodium borohydride has been proposed by Borch.[27] However, the imine intermediate was not observed, indicating that the imine must be reduced much faster than the imidate.

In the present investigation, reduction of the imidate $[Cu(L1)]^{2+}$ with $NaBH_4$ in deficiency resulted in the isolation of the enamine complex $[Cu(L2)]^{2+}$, which upon further reduction gave the fully reduced macrocycle. A mechanism based on the behavior of imidates under reducing conditions is given in Scheme V. The equilibrium for imine–enamine systems normally lies in favor of the imine,[28] but in the present system the strain energy associated with formation of 120° bond angles at the coordinated imine is enough to shift the balance toward the enamine.

(c) Hydrolysis of the Imidate. In the present system, the hydrolysis in basic media gives the expected amide **8** and methanol is also considered to be produced. Unlike typical imidates, *no* hydrolysis is observed at low pH, as attested by the fact that the imidate $[Cu(L1)]^{2+}$ may be recrystallized from hot 1 M $HClO_4$ with no noticeable decomposition. The coordination of the imidate nitrogen prevents its protonation, thereby inhibiting the acid-catalyzed hydrolysis pathway.

Amide complex ion **8** was characterized with IR (C=O stretch at 1577 cm^{-1}) and through the isolation of the free ligand **10** (see the Experimental Section). When the imidate was hydrolyzed in the presence of Na_2S, CuS precipitated from the solution, and the ligand was extracted into CH_2Cl_2. The ^{13}C NMR spectrum

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[26] Neilson, D. G. In *The Chemistry of Amidines and Imidates*; Patai, S., Ed.; Wiley Interscience: New York, 1975; pp 385–489.

[27] Borch, R. F. *Tetrahedron Lett.* **1968**, 61.

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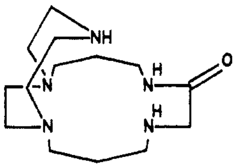

10

contained 14 lines, including a carbonyl carbon at 172 ppm (see Figure 3), as expected from the asymmetry of the ligand. The two signals around 25 ppm were due to the two central carbon atoms of the trimethylene groups. The mass spectrum is also in agreement with the proposed structure.

Conclusions

Complete reduction to the macrobicyclic complex $Cu(L3)^{2+}$ results in an ion of exceptional stability. There is no tendency toward hydrolysis even after 14 days in 4 M $HClO_4$. Indeed, the only method of removal of the metal ion is to react with Na_2S in a manner similar to that used in the preparation of the uncoordinated amide.

Investigations of this type are important in that examples are provided of the influence that metal-ion coordination can exert on the nature of the products isolated from a reaction sequence involving a series of finely tuned equilibria. Further study of the base-catalyzed hydrolysis of the imine-carbinolamine intermediate is underway since this represents a useful route to the synthesis of monooxo macrocyclic ligands.

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Supplementary Material Available: Tables S1-S13, containing anisotropic temperature parameters, selected intermolecular distances, hydrogen atom fractional atomic coordinates and isotropic temperature parameters, interatomic distances and bond angles involving the hydrogen atoms, mean plane calculations, fractional atomic coordinates and temperature parameters, and experimental crystallographic data for both complexes and hydrogen bonds for $[Cu(L2)](ClO_4)_2$ (14 pages); Tables S14 and S15, listing calculated and observed structure factors (19 pages). Ordering information is given on any current masthead page.

Alternate Coordination Modes of $(CF_3)_2C(OH)_2$: Synthesis and Structure of Five-Coordinate Ni^{2+} and Cu^{2+} Complexes Derived from a Chelating *gem*-Diol[1]

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Abstract: Two modes of coordination of hexafluoropropane-2,2-diol to transition-metal ions (Ni^{2+}, Cu^{2+}, Mn^{2+}, Co^{3+}, Pd^{2+}, Pt^{2+}) have been found. The diionized *gem*-diol can form a four-membered chelate ring with amine or phosphine coligands to give neutral complexes $L_n\overline{MOC(CF_3)_2O}$. Alternatively, two molecules of the diol may condense to give a six-membered chelate ring $L_n\overline{MOC(CF_3)_2OC(CF_3)_2O}$. By suitable choice of coligands L, the central metal ion may be four-, five-, or six-coordinate. The two types of ring system are not in equilibrium, and the formation of the four-membered ring is favored by bulkier coligands. It is suggested that the six-membered chelate ring is formed by template condensation between two alkoxide ligands on the metal. A complete structural determination has been made on the Ni^{2+} and Cu^{2+} complexes with the tridentate macrocycle 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene as coligand. Both contain a four-membered chelate ring and are formulated as the five-coordinate species $(\overline{NNN})\overline{MOC(CF_3)_2O}$ (**5**, M = Cu; **6**, M = Ni). The crystals are both isomorphic and isostructural, and they have orthorhombic symmetry in space group *Pbca* with $Z = 8$. Cell dimensions are as follows: **5**, $a = 20.520$ (3) Å, $b = 15.760$ (5) Å, $c = 14.380$ (5) Å, $V = 4650$ (3) Å^3; **6**, $a = 20.462$ (4) Å, $b = 15.759$ (3) Å, $c = 14.398$ (3) Å, $V = 4643$ (3) Å^3. Full-matrix least-squares refinement on F of 205 variables with 2176 and 2112 unique observations converged at conventional agreement factors of 0.043 and 0.047 for **5** and **6**, respectively. In each crystal, a pair of complex molecules linked by pairs of water molecules sits on a crystallographic center of symmetry. One alkoxide oxygen atom is hydrogen bonded to the two water molecules, and the other to an ethanol molecule of solvation. The metal atom is in approximate square-pyramidal coordination; the axial bond in **5** is lengthened by a Jahn-Teller distortion. The chelating *gem*-diol ligand in **5** and **6** forms almost planar rings, with bite angles of 68.4 (1)° and 67.1 (1)°, respectively.

Only in a limited number of cases is a *gem*-diol stable with respect to elimination of water, and there are even fewer reported cases of metal alkoxides formed from such systems. Aldehydes RCHO add water to give $RCH(OH)_2$ where R is H or an electronegative group, such as CF_3 or CCl_3. In an unusual example of a stable alkoxide of $CH_2(OH)_2$, Day et al. have determined the structure of the polyoxomolybdate cluster $[(CH_2O_2)Mo_4O_{13}H]^{3-}$; the $CH_2O_2^{2-}$ unit is situated above four coplanar molybdenum atoms with each alkoxide bridging between two metal atoms at a Mo-O distance of 2.194 (5) Å.[2] They note that $CH_3CH(OH)_2$, $C_6H_5CH(OH)_2$, and $CF_3CH(OH)_2$ form similar adducts, but $(CF_3)_2C(OH)_2$ does not. A brief report has been made of the platinum complex $(Ph_3P)_2\overline{PtOC(CH_3)_2O}$; it is of limited stability and has not been fully characterized.[3]

For trichloroacetaldehyde, the hydrate $CCl_3CH(OH)_2$ is familiar, but there is little reported work on its metal complexes.

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