Registry No. $Cu^{II}(H_{-3}G_4)^{2-}$, 57603-18-6; $\cdot Br_2^-$, 68565-50-4; $\cdot OH$, 3352-57-6; $\cdot CH_2OH$, 2143-68-2; $\cdot CO_2^-$, 34496-91-8; $(CH_3)_2\dot{C}OH$, 7277-18-1; $\cdot CH_2C(CH_3)_2OH$, 5723-74-0; $\cdot CH_2CO_2^-$, 19513-45-2; $\cdot CH_2CH(OH)CH_3$, 7277-18-1.

Notes

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Molecular Structure of Dichloro(1,4,7-triazacyclononane)copper(II), a Macrocyclic Triamine Complex with an Unusually Small Formation Constant

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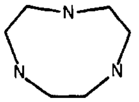
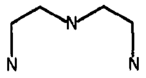
The title complex, $Cu([9]aneN_3)Cl_2$ (**1**), behaves anomalously with regard to the well-known macrocyclic effect. Typically, macrocyclic polyamine Cu(II) complexes exhibit larger formation constants than those of corresponding linear polyamines.[2] However, the formation constant of **1** ($\log K \approx 16$) is smaller than that of $Cu(dien)^{2+}$ ($\log K = 18.0$).[2,3]



$[9]aneN_3$



dien

In contrast, formation constants of $Ni([9]aneN_3)^{2+}$ and $Zn([9]aneN_3)^{2+}$ ($\log K = 16.2$ and 11.6, respectively) are substantially larger than those of $Ni(dien)^{2+}$ and $Zn(dien)^{2+}$ ($\log K = 10.7$ and 8.9, respectively).[3] The anomalous behavior of **1** has been attributed[2,3] to steric requirements of Cu(II) which have been frustrated in part by structural constraints of the $[9]aneN_3$ ligand. The present study was undertaken to help understand these constraints.[4]

Experimental Section

Preparation of 1. 1,4,7-Triazacyclononane trihydrochloride ($[9]aneN_3\cdot 3HCl$) was prepared by appropriate modification of a published procedure for 1,5,9,13-tetraazacyclohexadecane.[5] Evaporation of a solution of $[9]aneN_3\cdot 3HCl$ (5 mmol, 1.24 g), $CuCl_2$ (5 mmol, 0.85 g), and 15 mL of 1 N sodium hydroxide yielded sodium chloride crystals and large blue plates of **1** which were separated manually and recrystallized from water to yield pure **1**.

Anal. Calcd for $C_6H_{15}N_3CuCl_2$: C, 27.33; H, 5.73; N, 15.94; Cu, 24.10. Found: C, 27.33; H, 6.10; N, 15.88; Cu, 24.06.

Table I. Crystal Data and Data Collection Details

formula	$Cu(CH_2CH_2NHCH_2CH_2\text{-}NHCH_2CH_2NH)Cl_2$
mol wt	263.66
a, Å	7.428 (2)
b, Å	9.865 (2)
c, Å	6.932 (2)
α, deg	77.89 (2)
β, deg	99.12 (2)
γ, deg	92.61 (2)
space group	$P\bar{1}$
Z	2
no. of reflcns used to determine cell constants	13
d_{calcd}, g/cm³	1.786
d_{obsd}, g/cm³	1.76 (5)
λ(Cu Kα), Å	1.5418
filter	Ni
linear abs coeff, cm^{-1}	77.0
cryst dimens, mm	0.10 × 0.45 × 0.22
abs factor range	1.903–3.647
diffractometer	Syntex $P2_1$
data collectn method	θ–2θ
2θ range, deg	$4 \leq 2\theta \leq 110$
temp, °C	23 (1)
scan rate,[a] deg/min	1.5
scan range, deg	$2\theta(K\alpha_1) - 1$ to $2\theta(K\alpha_2) + 1$
no. of std reflcns	3
variation in std intens	±4.5%
no. of unique data collected	1239
no. of data used in refinement ($F^2 \geq 3\sigma(F^2)$)	1182
data:parameter ratio	8.0
final R_F[b]	0.031
final R_{wF}[c]	0.036

[a] Background measurements were made at the beginning and end of each scan; the total time for background counting was equal to the scan time. [b] $R_F = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. [c] $R_{wF} = [\Sigma w(|F_o - F_c|)^2 / \Sigma w F_o^2]^{1/2}$.

X-ray Diffraction Studies. Crystal data and data collection and refinement details are given in Table I. Intensity data were collected and corrected for decay, *Lp* effects, and absorption as described previously.[6] Diffractometer examination of the reciprocal lattice revealed no systematic absences.

The structure was solved[7] by direct methods and refined successfully in space group $P\bar{1}$ by using full-matrix least-squares techniques. Neutral atom scattering factors were used, and anomalous dispersion corrections were applied to all nonhydrogen atoms.[8] An *E* map, calculated from the starting set having the highest combined figure of merit, revealed the Cu and Cl atoms. All remaining nonhydrogen atoms were located on a subsequent difference Fourier map. Several

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(1) (a) Rutgers University, New Brunswick. (b) Rutgers University, Newark.

(2) Kodama, M.; Kimura, E. *J. Chem. Soc., Dalton Trans.* **1977**, 1473–8 and references cited therein.

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(7) In addition to local programs for the IBM 370/168 computer, local modifications of the following programs were used: LPCOR Lp and absorption program; Zalkin's FORDAP Fourier program; Johnson's ORTEPII thermal ellipsoid plotting program; Busing, Martin, and Levy's ORFFE error function program; Main, Lessinger, Declercq, Woolfson, and Germain's MULTAN 74 program for the automatic solution of crystal structures; the FLINUS least-squares program obtained from Brookhaven National Laboratory.

(8) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 72–98, 148–51.

Table II. Fractional Atomic Coordinates and Thermal Parameters[a]

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.49728 (9)	0.23094 (7)	0.2169 (1)	9.8 (1)	57.7 (8)	13.6 (2)	1.8 (8)	2.9 (1)	−18.8 (9)
Cl(1)	0.7577 (2)	0.3232 (1)	0.3581 (2)	10.4 (2)	116 (2)	21.9 (3)	−21 (2)	3.1 (2)	−59 (2)
Cl(2)	0.6253 (2)	0.1842 (1)	−0.0448 (2)	16.3 (3)	86 (2)	18.8 (3)	−4 (2)	7.5 (5)	−43 (2)
N(1)	0.3077 (6)	0.4097 (6)	0.0913 (6)	12.1 (9)	66 (5)	16 (1)	14 (5)	2.3 (8)	−5 (6)
N(2)	0.3817 (5)	0.2245 (4)	0.4703 (6)	10.4 (8)	75 (5)	13 (1)	−1 (5)	1.9 (7)	−21 (6)
N(3)	0.2700 (5)	0.1179 (4)	0.1429 (6)	11.9 (8)	65 (5)	16 (1)	−9 (5)	4.6 (7)	−43 (6)
C(1)	0.1336 (7)	0.3496 (6)	0.0068 (9)	10 (1)	97 (7)	17 (1)	12 (7)	0 (1)	−24 (8)
C(2)	0.1630 (8)	0.2065 (6)	−0.0313 (8)	13 (1)	113 (8)	16 (1)	−4 (7)	1 (1)	−56 (8)
C(3)	0.1681 (7)	0.0689 (6)	0.3143 (8)	14 (1)	75 (7)	19 (1)	−24 (7)	7 (1)	−37 (8)
C(4)	0.2810 (8)	0.0911 (5)	0.5049 (8)	16 (1)	66 (6)	18 (1)	−6 (7)	7 (1)	−8 (8)
C(5)	0.2642 (7)	0.3467 (5)	0.4455 (8)	13 (1)	73 (6)	17 (1)	3 (7)	3 (1)	−49 (8)
C(6)	0.3015 (8)	0.4625 (5)	0.2739 (8)	13 (1)	63 (6)	20 (1)	10 (7)	1 (1)	−39 (8)

	x	y	z	B, Å^2		x	y	z	B, Å^2
H(N1)	0.33 (1)	0.479 (7)	0.01 (1)	3.7	H2(C3)	0.128 (9)	−0.034 (7)	0.34 (1)	4.0
H(N2)	0.469 (9)	0.221 (7)	0.58 (1)	3.4	H1(C4)	0.20 (1)	0.092 (7)	0.60 (1)	4.1
H(N3)	0.300	0.041	0.109	3.5	H2(C4)	0.36 (1)	0.027 (8)	0.55 (1)	4.1
H1(C1)	0.092 (9)	0.403 (7)	−0.12 (1)	4.1	H1(C5)	0.137 (9)	0.302 (7)	0.43 (1)	3.8
H2(C1)	0.04 (1)	0.351 (7)	0.09 (1)	4.1	H2(C5)	0.276 (9)	0.368 (7)	0.56 (1)	3.8
H1(C2)	0.05 (1)	0.167 (7)	−0.07 (1)	4.2	H1(C6)	0.21 (1)	0.532 (7)	0.25 (1)	4.0
H2(C2)	0.238 (9)	0.232 (7)	−0.15 (1)	4.2	H2(C6)	0.41 (1)	0.507 (7)	0.30 (1)	4.0
H1(C3)	0.07 (1)	0.123 (7)	0.29 (1)	4.0					

[a] Values for β_{22}, β_{12}, and β_{23} are $\times 10^4$; other values are $\times 10^3$. The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

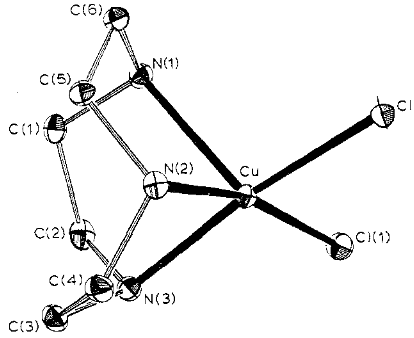

Figure 1. View of Cu([9]aneN$_3$)Cl$_2$ showing the atom numbering scheme.

cycles of anisotropic refinement reduced R_F to 0.053. All H atoms were located on a difference map and assigned temperature factors of $B_H = B_N + 1$, where N is the atom bonded to H. Inclusion of H atoms reduced R_F to 0.032 while unit weight refinement of all atom coordinates except H(N3)[9] and anisotropic temperature factors for all nonhydrogen atoms gave final values of 0.031 and 0.036 for R_F and R_{wF}, respectively.

For the final cycle, nonhydrogen parameter changes were $<0.4\sigma$ and H parameter changes were $<1\sigma$, where σ is the esd obtained from the inverse matrix. A final difference map revealed no significant features. Final parameters are listed in Table II. A list of observed and calculated structure factors is available.[10]

Results and Discussion

The structure (Figure 1) contains discrete Cu(II) monomers with approximately square-pyramidal N$_3$Cl$_2$ ligand donor sets. The macrocyclic triamine is coordinated facially with N(2) and N(3) occupying equatorial positions and N(1) apically situated; chloride ions occupy the two remaining equatorial positions. Structural details (Table III) of the ligand coordination and of the ligand itself are similar to those reported[4] for Cu([9]aneN$_3$)Br$_2$.

Coordination of the macrocyclic triamine yields three linked five-membered chelate rings, each with the low-energy gauche conformation. The observed N–Cu–N bond angles [82.2 (2)–83.0 (2)°] are significantly smaller than those in reference complexes containing diamine ligands [for Cu(en)$_2$·2BF$_4$[11] the angle is 86.4 (5)° and for Cu(pn)$_2$·2ClO$_4$[12] 84.6 (2)°] and

Table III. Bond Distances (Å) and Angles (Deg)[a]

(A) Bond Distances within Metal Coordination Sphere

Cu–Cl(1)	2.268 (1)	Cu–N(2)	2.063 (4)
Cu–Cl(2)	2.312 (1)	Cu–N(3)	2.038 (4)
Cu–N(1)	2.246 (4)		

(B) Bond Distances within the Ligand

N(1)–C(1)	1.484 (7)	N(3)–C(3)	1.493 (6)
N(1)–C(6)	1.474 (7)	C(1)–C(2)	1.521 (8)
N(2)–C(4)	1.478 (6)	C(3)–C(4)	1.500 (8)
N(2)–C(5)	1.486 (6)	C(5)–C(6)	1.517 (7)
N(3)–C(2)	1.473 (7)		

(C) Bond Angles with Cu as Vertex

Cl(1)–Cu–Cl(2)	94.23 (5)	Cl(2)–Cu–N(2)	167.0 (1)
Cl(1)–Cu–N(1)	105.8 (1)	Cl(2)–Cu–N(3)	91.0 (1)
Cl(1)–Cu–N(2)	90.5 (1)	N(1)–Cu–N(2)	83.0 (2)
Cl(1)–Cu–N(3)	168.2 (1)	N(1)–Cu–N(3)	82.6 (2)
Cl(2)–Cu–N(1)	107.2 (1)	N(2)–Cu–N(3)	82.2 (2)

(D) Bond Angles with N as Vertex

Cu–N(1)–C(1)	106.3 (3)	C(4)–N(2)–C(5)	113.2 (4)
Cu–N(1)–C(6)	99.9 (3)	Cu–N(3)–C(2)	105.7 (3)
C(1)–N(1)–C(6)	115.1 (4)	Cu–N(3)–C(3)	112.5 (3)
Cu–N(2)–C(4)	106.1 (3)	C(2)–N(3)–C(3)	114.1 (4)
Cu–N(2)–C(5)	110.7 (3)		

(E) Bond Angles with C as Vertex

N(1)–C(1)–C(2)	110.9 (4)	N(2)–C(4)–C(3)	110.3 (4)
N(3)–C(2)–C(1)	111.8 (4)	N(2)–C(5)–C(6)	112.8 (4)
N(3)–C(3)–C(4)	110.3 (4)	N(1)–C(6)–C(5)	111.4 (4)

[a] Distance and angle data are given for all nonhydrogen atoms. A list of bond distances and angles involving hydrogen atoms is available.[10]

Table IV. Possible Hydrogen-Bonding Distances (Å) and Angles (Deg)

donor (D)	hydrogen (H)	acceptor (A)	D–H···A	D···A	H···A	D–H
N(1)	H(N1)	Cl(1)^{i} [a]	152 (6)	3.616 (4)	2.85 (6)	0.84 (7)
N(2)	H(N2)	Cl(2)^{ii}	160 (6)	3.508 (4)	2.65 (6)	0.90 (7)
N(3)	H(N3)	Cl(2)^{iii}	175	3.344 (4)	2.46	0.89

[a] i = $1-x, 1-y, -z$; ii = $x, y, 1+z$; iii = $1-x, -y, -z$.

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(9) The coordinates of this atom refined poorly; consequently, they were set to the values obtained from the difference Fourier map and not refined.

(10) Supplementary material.

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indicate that the chelate rings in **1** are somewhat strained.

The Cu atom is displaced 0.2 Å from the equatorial plane defined by N(2), N(3), Cl(1), and Cl(2) in the direction of N(1). The Cu–Cl lengths are nonequivalent and are typical for equatorial Cu–Cl bonding.[13,14] This inequality may result from intermolecular hydrogen bonding (Table IV); Cl(2), with the longer Cu–Cl distance, participates in two relatively strong hydrogen bonds with amine H atoms, while Cl(1) participates in only one. The equatorial Cu–N bonds are approximately equal (2.063 (4), 2.038 (4) Å) and compare well with the values reported[4] for Cu([9]aneN$_3$)Br$_2$ (2.046 (4), 2.047 (4) Å) and for an ethylenediamine complex of Cu(II)[15] containing equatorial CuN$_2$Cl$_2$ units (2.054 (4), 2.081 (3) Å). The apical Cu–N(1) distance (2.268 (1) Å), while slightly longer than that in Cu([9]aneN$_3$)Br$_2$ (2.230 (4) Å) and substantially longer than the equatorial Cu–N bonds, may, as noted previously,[4] be anomalously shortened due to constraint by the macrocyclic triamine which causes the Cu–N(apical) bond to be tilted toward the basal N atoms.

In our view, the most significant feature of the structure is the elongated Cu–N(1) bond, a feature which is not common to all metal structures containing macrocyclic triamine ligands. Thus, bis[(*R*)-2-methyl-1,4,7-triazacyclononane]cobalt triiodide pentahydrate[16] and bis(isothiocyanato)(2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene)nickel(II)[17] contain nearly equal metal–N(macrocyclic) bonds within each complex, while μ-carbonato-bis(2,4,4,7-tetramethyl-1,5,9-triazacyclododec-1-ene)dicopper diperchlorate,[18] with a CuN$_3$O$_2$ unit structurally similar to that in **1**, exhibited substantially different equatorial (1.961 (7), 1.977 (7) Å) and apical (2.195 (7) Å) Cu–N distances.

A structural basis for the small formation constant of **1** is revealed by comparing the results reported here with those for (oxalato)(diethylenetriamine)copper(II)[19] tetrahydrate which contains approximately square-pyramidal CuN$_3$O$_2$ units with an apical O donor. Relative to **1**, the Cu–N distances are short (2.009 (8), 2.021 (7), 1.996 (8) Å) and the N–Cu–N angles are unstrained (85.2 (3), 85.0 (3)°). Thus, the flexible dien ligand achieves relatively strain-free meridional coordination with full equatorial Cu–N bonding.[20] In **1**, Cu–N bonding is attenuated by strain within the chelate rings and by the weak Cu–N interaction. These structural effects may be associated with thermodynamic and spectroscopic results reported for Cu(triamine)$^{2+}$(aq) complexes. Weaker Cu–N bonding in Cu([9]aneN$_3$)$^{2+}$(aq) relative to Cu(dien)$^{2+}$(aq) is consistent both with the respective $\Delta H°$ values of -13.0[2] and -18.0[21] kcal/mol and with the $\sim$1000-cm^{-1} red shift[2] in the Cu(II) d,d transition of Cu([9]aneN$_3$)$^{2+}$(aq) relative to Cu(dien)$^{2+}$(aq).

Acknowledgment. This work was supported by a research grant (AM 16412 to H.J.S.) from the National Institutes of Health and by a grant of computing time from the Rutgers Computing Center.

Registry No. 1, 73002-72-9.

Supplementary Material Available: Tables of observed and calculated structure factor amplitudes and bond distances and angles involving H atoms (7 pages). Ordering information is given on any current masthead page.

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Electron Spin Resonance Studies of Some Ruthenium(III) Complexes

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The low-spin d^5 configuration is a good probe of molecular structure and bonding since the observed *g* values are very sensitive to small changes in the structure and to the metal–ligand covalency. Although a large number of d^5(t$_{2g}{}^5$) complexes have been studied, the application of electron spin resonance was mainly limited to the first-row transition series. Very few ruthenium(III) complexes have been subjected to ESR studies.[1-4]

In this paper we report an ESR study of a number of low-spin ruthenium(III) complexes containing triphenylarsine, triphenylphosphine, and β-diketonate (β-dk) ligands. Their geometries, ground states, and other spectral parameters have been obtained by using the ligand field theory for low-spin d^5 systems.

Experimental Section

The complexes studied in this work were prepared by the method already reported in the literature.[5-9] Tribromobis(triphenylarsine)ruthenium(III)–methanol [RuBr$_3$(AsPh$_3$)$_2$·CH$_3$OH] was prepared by the addition of methanol to a solution of RuBr$_3$(AsPh$_3$)$_3$ in dichloromethane and recrystallized from CH$_2$Cl$_2$–CH$_3$OH (yield 90%).

Reaction of RuX$_2$(β-dk)L$_2$ with Pyridine. An excess of pyridine (1–2 mL) was added to a solution of RuX$_2$(β-dk)L$_2$ (0.5 mmol) in 40 mL of CH$_2$Cl$_2$, and the resultant solution was heated to 70–80 °C for about 6–7 min. The solution was cooled, and an excess of methanol was added to get bright red crystals which were recrystallized from CH$_2$Cl$_2$–CH$_3$OH.

The complexes on analyses fit to a molecular formula RuX$_2$(β-dk)L(py) (yield 90%).

EPR Spectra. EPR spectra of the powdered samples and of the samples in CHCl$_3$ solution were recorded with a Varian Associates

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