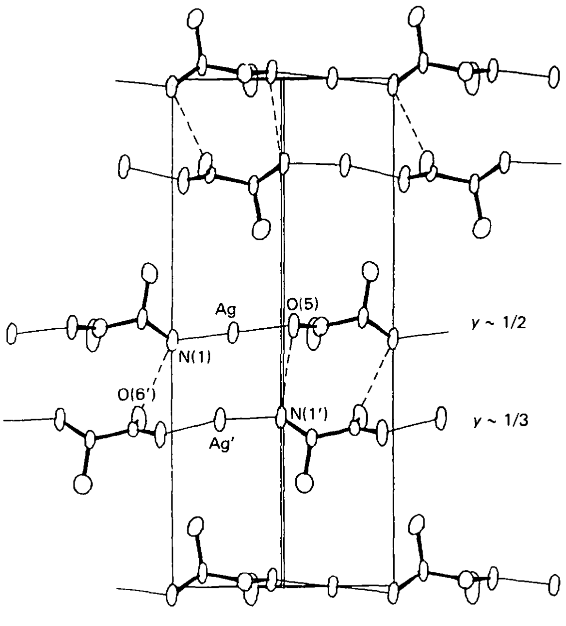

Fig. 2. Les liaisons hydrogène interchaînes.

N(1')···O(5')$_{001}$ = 2,94 (1) Å [la notation $X(n)_{pqr}$ signifie que la translation $p\mathbf{a} + q\mathbf{b} + r\mathbf{c}$ est appliquée aux coordonnées de l'atome $X(n)$ du Tableau 1]; il en résulte la formation de couches perpendiculaires à l'axe *b*. Les couches AgAla et Ag'Ala' sont reliées deux à deux par liaison hydrogène entre les atomes O(5) et N(1'), d'une part [O(5)···N(1')$^{ii}_{1\bar{1}1}$ = 3,12 (1) Å] [(ii): l'opération de symétrie $-x, \frac{1}{2}+y, -z$ est appliquée aux coordonnées du Tableau 1] et entre les atomes N(1) et O(6'), d'autre part [N(1)···O(6')$^{ii}_{1\bar{1}1}$ = 2,94 (1) Å] (Fig. 2). La cohésion entre les 'bicouches' ainsi obtenues est assurée par des liaisons du type van der Waals; les plus importantes ont lieu entre les atomes C(3) et O(5')$_{101}$ [3,42 (2) Å] et entre les atomes O(5) et C(3') [3,52 (2) Å].

Les atomes d'azote échangent donc deux liaisons hydrogène, l'une reliant deux molécules AgAla (ou Ag'Ala') et l'autre reliant une molécule AgAla et une molécule Ag'Ala'; les angles entre les liaisons hydrogène valent respectivement: 116,7 (6)° pour N(1) [O(5)$_{100}$···N(1)···O(6')$^{ii}_{1\bar{1}1}$] et 94,0 (5)° pour N(1') [O(5')$_{001}$···N(1')···O(5)$^{ii}_{101}$].

Références

Acland, C. B. & Freeman, H. C. (1971). *J. Chem. Soc.* pp. 1016–1017.

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.

Démaret, A. (1986). Thèse d'Etat, Univ. de Paris VII.

Démaret, A. & Abraham, F. (1987). *Acta Cryst.* Sous presse.

Hill, C., Starcher, B. & Matrone, G. (1964). *J. Nutr.* **83**, 107–110.

Krishna, J. & Rao, M. (1968). *Indian J. Pure Appl. Phys.* **6**, 51–53.

Krishnan, R. S., Rao, J. K. M. & Viswamitra, M. A. (1970). *J. Phys. Soc. Jpn*, **28**, 298–300.

Prewitt, C. T. (1966). *SFLS-5. A Fortran* IV *Full-Matrix Crystallographic Least-squares Program.* Rapport ORNL-TM-305. Oak Ridge National Laboratory, Tennessee, E.-U.

Acta Cryst. (1987). C**43**, 1521–1524

Structure of *trans*-(Aqua)bis(dimethylglyoximato)pyridinecobalt(III) Nitrate Monohydrate

By M. W. Attia,* E. Zangrando and L. Randaccio†

Dipartimento di Scienze Chimiche, Università di Trieste, 34127 *Trieste, Italy*

and C. Lopéz

Chemistry Department, Emory University, Atlanta, Georgia 30322, *USA*

(*Received* 11 *February* 1987; *accepted* 21 *April* 1987)

Abstract. $[\mathrm{Co(C_4H_7N_2O_2)_2(C_5H_5N)(H_2O)}]^+.\mathrm{NO_3^-}.\mathrm{H_2O}$, $M_r = 466{\cdot}3$, monoclinic, $P2_1/n$, $a = 10{\cdot}502$ (3), $b = 15{\cdot}118$ (3), $c = 12{\cdot}587$ (3) Å, $\beta = 102{\cdot}14$ (2)°, $V = 1953{\cdot}9$ (8) Å^3, $Z = 4$, $D_x = 1{\cdot}58$ Mg m^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0{\cdot}7107$ Å, $\mu = 0{\cdot}98$ mm^{-1}, $F(000) = 968$, $T = 293$ K, $R = 0{\cdot}045$ for 2673 unique observed reflections. The $[\mathrm{pyCo(DH)_2OH_2}]^+$ cation (DH = dimethylglyoximate monoanion) is characterized by

---

* On leave from the Physics Department, Suez Canal University, Ismailia, Egypt.

† To whom all correspondence should be addressed.

0108-2701/87/081521-04$01.50

the shortest Co—OH_2 [1·916 (3)] and Co—py [1·926 (3) Å] axial distances so far reported in cobaloximes. The two DH units make a dihedral angle, α, of 8·1 (2)° and bend towards the H_2O axial ligand. Comparison with available data suggests that water is the weakest σ-donor and the least bulky ligand so far reported in structurally characterized cobaloximes, while py is a very weak σ-donor ligand, even weaker than N_3, but a relatively bulky ligand.

Introduction. Cobaloximes [the trivial name of the LCo(DH)$_2X$ complexes, where DH = the monoanion of dimethylglyoxime, and L and X are neutral and monoanion ligands respectively] represent one of the most extensively studied class of metal compounds. In fact, organometallic cobaloximes (X=R) are well known vitamin B_{12} models. On the other hand, the whole series of compounds forms a very flexible system for studying the interrelationship between steric and electronic effects which influence the properties of these complexes both in solution and in the solid state (Bresciani-Pahor, Forcolin, Marzilli, Randaccio, Summers & Toscano, 1985). Recent results (Zangrando, Bresciani-Pahor, Randaccio, Charland & Marzilli, 1986) have shown that the σ-donor power of the alkyl group in the pyCo(DH)$_2R$ series clearly influences kinetic, spectroscopic and structural features of these complexes and a quantitation of their interrelationship has been proposed. As part of a programme aimed at obtaining further insight into these problems, we report the structure of [pyCo(DH)$_2$-OH_2]$NO_3.H_2O$ (I), where the H_2O ligand is expected to have a very low σ-donor ability. Thus the Co—py bond length should represent the minimum distance between py and Co.

Experimental. Crystal 0·2 × 0·2 × 0·35 mm, Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Mo$K\alpha$ radiation, lattice constants by least-squares refinement of 25 setting-angles reflections with $16 < \theta < 20°$, three standard reflections (1,2,10, 713, $\bar{1},\bar{1}$,10) measured every 4000 s, no significant drift noted; $\omega/2\theta$ scan, scan angle $(1·2 + 0·35\tan\theta)°$; 5086 reflections measured in the range $3 \le \theta \le 28°$, $-13 \le h \le 13$, $0 \le k \le 20$, $0 \le l \le 16$, 2673 observed reflections [$I \ge 3\sigma(I)$] used for structure determination, space group from systematic absences, intensities corrected for Lorentz–polarization effects but not for absorption because of the small crystal size and low μ value. Structure solved by Patterson method, Fourier synthesis and full-matrix least squares on F, 262 parameters refined, anisotropic temperature factors for all non-hydrogen atoms, H atoms fixed at calculated geometrical positions except for the water molecules, for which the H atoms have been located from a ΔF map, with isotropic B ($B = 1·3 \times B_{eq}$ of the atom to which they are attached), $R = 0·045$, $wR = 0·054$, $S = 1·313$, $w = 1/[\sigma(F_o)^2 + (0·2F_o)^2 + 1]$; max. $\Delta/\sigma = 0·04$, the final difference map had a maximum of 0·39 and a minimum of 0·35 e Å^{-3}, complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974), no correction for secondary extinction, all computer programs used were those in the Enraf–Nonius *SDP* (Frenz, 1981) on a PDP 11/44 computer. The atomic positional parameters derived from the last cycle of refinement are listed in Table 1. Interatomic distances and angles are reported in Table 2.*

Discussion. An *ORTEP* (Johnson, 1965) drawing of the asymmetric part of the unit cell with the atom-numbering scheme is shown in Fig. 1. The crystal is built up of [pyCo(DH)$_2OH_2$]$^+$ cations, NO_3^- anions and water molecules of crystallization. In addition to the electrostatic interactions, a hydrogen-bond network involves all three species. The hydrogen-bond scheme (Fig. 2) is characterized by two relatively short contacts of O5, coordinated to cobalt, with O9 [2·562 (5) Å] and with the nitrate O8 atom [2·700 (6) Å]. The O8···O5···O9 angle is 108·1 (2)°. Two longer hydrogen bonds of O9 with O3 [2·798 (5) Å] of the unit at $-x$, $-y$, $1-z$ and with the nitrate O7 atom [2·850 (6) Å] of the unit at $-x-\frac{1}{2}$, $y+\frac{1}{2}$, $\frac{1}{2}-z$ complete the scheme. The angle O3···O9···O7 is 111·5 (2)°. This scheme shows that the two H atoms attached to O5 are involved in the short bonds and those attached to O9 in the long ones, as also suggested by the location of hydrogen in the ΔF map. The intramolecular hydrogen bonds of the two oxime bridges are significantly different, the O1···O4 and O2···O3 distances being 2·481 (4) and 2·543 (4) Å respectively. The difference is due to the involvement of O3 in the intermolecular hydrogen bond with O9. The nitrate ions undergo a relatively high thermal motion as shown by their B_{eq}'s and the N6—O8 distance of 1·243 (5) Å is slightly longer than the N6—O6 and N6—O7 distances which are both 1·206 (6) Å. The geometry is strictly planar with angles at N ranging from 117·5 (5) to 122·6 (5)°. The [pyCo(DH)$_2OH_2$]$^+$ cation is characterized by a distorted octahedral geometry of the Co atom (Fig. 1). The four equatorial N atoms are coplanar within ±0·015 (3) Å with Co displaced by 0·041 Å out of their mean plane towards py. The two DH units, planar within ±0·027 (6) Å, make a dihedral angle, α, of 8·1 (2)°, and bend towards the axial water molecule. The dihedral angle between the planes passing through the N1—C2—C3—N2 and N3—C6—

---

* Lists of structure factors, anisotropic thermal parameters for non-hydrogen atoms and positional parameters for hydrogen atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43987 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

C7—N4 groupings is 5·7 (2)°. The pyridine molecule has the usual orientation found in cobaloximes, its mean plane crossing the oxime bridges. The axial fragment is characterized by Co—N and Co—O distances of 1·926 (3) and 1·916 (3) Å, respectively. These values correspond to the shortest Co—py and Co—OH_2 bonds so far reported. The Co—OH_2 distance is only slightly longer than those of 1·897 (7) and 1·909 (3) Å reported for some peroxocobaloximes, $pyCo(DH)_2O_2R$ (Giannotti, Fontaine, Chiaroni & Riche, 1976). However, in the latter complexes the Co—py distances are 2·013 (7) and 1·994 (3) Å. The Co—OH_2 and some Co—py distances are compared in Table 3. Analysis of these data suggests that the water ligand is the weakest electron donor as well as the least bulky ligand so far reported in structurally characterized cobaloximes. On the other hand, pyridine is a very weak σ-donor ligand, even weaker than N_3, but a relatively bulky ligand.

Table 1. *Fractional positional parameters for non-hydrogen atoms with e.s.d.'s in parentheses and equivalent isotropic temperature factors*

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
Co	0·11612 (5)	0·16966 (3)	0·30945 (4)	2·342 (8)
O1	0·0318 (3)	0·2598 (2)	0·1089 (2)	3·98 (7)
O2	0·1836 (3)	0·2489 (2)	0·5235 (2)	4·03 (7)
O3	0·1943 (3)	0·0813 (2)	0·5101 (2)	4·24 (7)
O4	0·0252 (3)	0·0958 (2)	0·0999 (2)	4·14 (7)
O5	−0·0609 (3)	0·1649 (2)	0·3260 (3)	4·44 (7)
O6	−0·2242 (5)	0·3329 (3)	0·2650 (3)	7·6 (1)
O7	−0·2116 (5)	0·4265 (3)	0·3893 (4)	8·7 (1)
O8	−0·1805 (5)	0·2883 (3)	0·4255 (3)	7·7 (1)
O9	−0·1991 (4)	0·0238 (2)	0·3061 (3)	5·37 (9)
N1	0·0735 (3)	0·2690 (2)	0·2152 (3)	2·84 (7)
N2	0·1474 (3)	0·2620 (2)	0·4146 (3)	2·94 (7)
N3	0·1540 (3)	0·0712 (2)	0·4043 (3)	2·96 (7)
N4	0·0744 (3)	0·0791 (2)	0·2051 (3)	2·78 (7)
N5	0·2934 (3)	0·1725 (2)	0·2905 (2)	2·45 (6)
N6	−0·2066 (4)	0·3507 (3)	0·3603 (4)	4·48 (9)
C1	0·0447 (5)	0·4296 (3)	0·1992 (4)	4·5 (1)
C2	0·0830 (4)	0·3468 (3)	0·2602 (4)	3·19 (9)
C3	0·1266 (4)	0·3417 (3)	0·3787 (3)	3·19 (8)
C4	0·1433 (5)	0·4210 (3)	0·4510 (4)	4·7 (1)
C5	0·1490 (6)	−0·0904 (3)	0·4210 (4)	5·0 (1)
C6	0·1327 (4)	−0·0062 (3)	0·3595 (3)	3·26 (9)
C7	0·0852 (4)	−0·0013 (3)	0·2417 (3)	2·88 (8)
C8	0·0483 (5)	−0·0804 (3)	0·1717 (4)	4·5 (1)
C9	0·3210 (4)	0·1719 (3)	0·1909 (3)	3·11 (8)
C10	0·4471 (4)	0·1746 (3)	0·1749 (3)	3·72 (9)
C11	0·5490 (4)	0·1789 (3)	0·2630 (4)	4·0 (1)
C12	0·5209 (4)	0·1795 (3)	0·3649 (4)	4·0 (1)
C13	0·3946 (4)	0·1761 (3)	0·3767 (3)	3·02 (8)

Table 2. *Bond distances* (Å) *and angles* (°)

Co—O5	1·916 (3)	N3—C6	1·298 (5)
Co—N1	1·907 (4)	N4—C7	1·298 (4)
Co—N2	1·903 (3)	N5—C9	1·345 (4)
Co—N3	1·898 (4)	N5—C13	1·351 (4)
Co—N4	1·884 (3)	C1—C2	1·480 (5)
Co—N5	1·926 (3)	C2—C3	1·467 (5)
O1—N1	1·326 (4)	C3—C4	1·494 (5)
O2—N2	1·358 (4)	C5—C6	1·481 (6)
O3—N3	1·319 (4)	C6—C7	1·463 (5)
O4—N4	1·340 (4)	C7—C8	1·486 (6)
O6—N6	1·206 (6)	C9—C10	1·381 (5)
O7—N6	1·206 (4)	C10—C11	1·371 (6)
O8—N6	1·243 (5)	C11—C12	1·375 (7)
N1—C2	1·300 (5)	C12—C13	1·367 (5)
N2—C3	1·290 (5)		
O5—Co—N1	89·5 (1)	Co—N4—C7	116·3 (2)
O5—Co—N2	88·9 (1)	O4—N4—C7	121·1 (4)
O5—Co—N3	89·0 (1)	Co—N5—C9	121·3 (2)
O5—Co—N4	87·7 (1)	Co—N5—C13	121·2 (2)
O5—Co—N5	178·8 (1)	C9—N5—C13	117·5 (4)
N1—Co—N2	80·7 (1)	O6—N6—O7	120·4 (5)
N1—Co—N3	178·4 (1)	O6—N6—O8	117·0 (5)
N1—Co—N4	98·6 (1)	O7—N6—O8	122·6 (5)
N1—Co—N5	90·7 (1)	N1—C2—C1	123·6 (4)
N2—Co—N3	98·9 (1)	N1—C2—C3	112·0 (3)
N2—Co—N4	176·6 (1)	C1—C2—C3	124·3 (4)
N2—Co—N5	92·3 (1)	N2—C3—C2	113·5 (3)
N3—Co—N4	81·8 (1)	N2—C3—C4	123·2 (4)
N3—Co—N5	90·9 (1)	C2—C3—C4	123·3 (4)
N4—Co—N5	91·1 (1)	N3—C6—C5	123·9 (4)
Co—N1—O1	122·0 (2)	N3—C6—C7	112·7 (3)
Co—N1—C2	117·1 (3)	C5—C6—C7	123·3 (4)
O1—N1—C2	121·0 (3)	N4—C7—C6	113·1 (3)
Co—N2—O2	124·5 (2)	N4—C7—C8	123·4 (4)
Co=N2—C3	116·7 (3)	C6—C7—C8	123·4 (4)
O2—N2—C3	118·8 (3)	N5—C9—C10	122·6 (3)
Co—N3—O3	121·6 (2)	C9—C10—C11	119·5 (4)
Co—N3—C6	116·1 (3)	C10—C11—C12	118·1 (4)
O3—N3—C6	122·2 (3)	C11—C12—C13	120·3 (4)
Co—N4—O4	122·4 (2)	N5—C13—C12	122·2 (3)

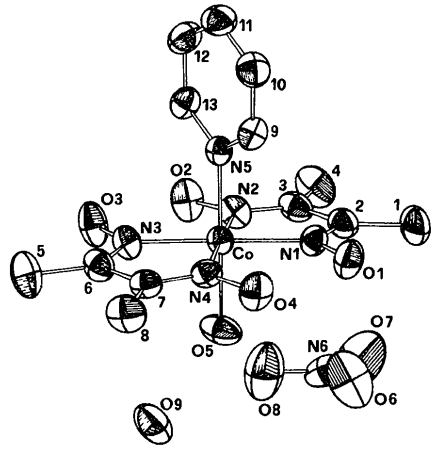

Fig. 1. *ORTEP* drawing (Johnson, 1965) and labeling scheme for non-hydrogen atoms of the title complex (thermal ellipsoids at 50% probability). The C atoms are labeled by their ordering number in the coordinate list.

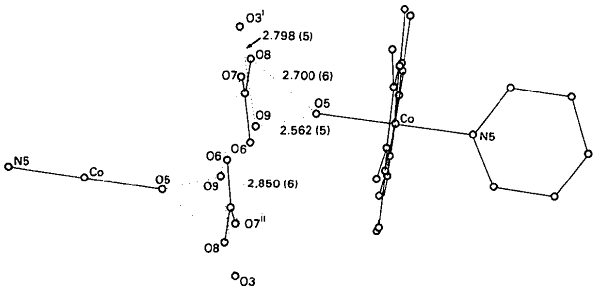

Fig. 2. Intermolecular hydrogen-bonding scheme. [Symmetry codes: (i) $-x, -y, 1-z$; (ii) $-\frac{1}{2}-x, y+\frac{1}{2}, \frac{1}{2}-z$.]

Table 3. *Comparison of* Co–$O(OH_2)$ *and* Co–N(py) *distances* (Å) *in cobaloximes* $H_2OCo(DH)_2X$ *and* $pyCo(DH)_2X$ [α *bendings* (°) *in pyridine complexes are also reported*]

X	Co–O	X	Co–N	α*
py	1·916 (3)	H_2O	1·926 (3)	8·1
Br	1·96 (1)	py	1·946	—
NO_2	1·980 (5)	N_3	1·973 (1)	2·9
CN	1·992 (4)	O_2CMe_2Ph	1·994 (3)	—
Me	2·058 (3)	Me	2·068 (3)	3·2

All data are from Bresciani-Pahor, Forcolin, Marzilli, Randaccio, Summers & Toscano (1985) except those of the present work.

* Values of α indicate that the bending of the equatorial ligand is towards the group X.

This work was supported by an MPI grant (to LR); MWA has carried out this work with the support of the ICTP (Trieste) programme for training and research in Italian laboratories.

References

Bresciani-Pahor, N., Forcolin, M., Marzilli, L. G., Randaccio, L, Summers, M. F. & Toscano, P. J. (1985). *Coord. Chem. Rev.* **63**, 1–125.

Frenz, B. A. (1981). *Enraf–Nonius Structure Determination Package*, 4th ed., version 18. Enraf–Nonius, Delft, The Netherlands.

Giannotti, C., Fontaine, C., Chiaroni, A. & Riche, C. (1976). *J. Organomet. Chem.* **113**, 57–59.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Zangrando, E., Bresciani-Pahor, N., Randaccio, L., Charland, J. P. & Marzilli, L. G. (1986). *Organometallics*, **5**, 1938–1944.

Acta Cryst. (1987). C**43**, 1524–1527

The Aqua and the Perchlorato Copper(II) Complexes of *N,N'*-Bis(*β*-carbamoylethyl)-*N*-methylethylenediamine*

By Tian-Huey Lu,† Hsi-Chi Shan,† Min-Shiun Chao‡ and Chung-Sun Chung‡

Department of Physics and Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 30043

(*Received* 28 *January* 1987; *accepted* 18 *March* 1987)

Abstract. Aqua(4-methyl-4,7-diazadecanediamide)-copper(II) (4-methyl-4,7-diazadecanediamide)perchloratocopper(II) triperchlorate monohydrate, $[Cu(C_9H_{20}N_4O_2)(H_2O)][Cu(C_9H_{20}N_4O_2)(ClO_4)](ClO_4)_3.H_2O$, $M_r = 993{\cdot}5$, triclinic, $P\bar{1}$, $a = 12{\cdot}626$ (3), $b = 12{\cdot}891$ (2), $c = 13{\cdot}387$ (3) Å, $\alpha = 114{\cdot}19$ (2), $\beta = 82{\cdot}79$ (2), $\gamma = 107{\cdot}07$ (3)°, $V = 1900$ (1) Å^3, $Z = 2$, $D_m = 1{\cdot}731$ (7), $D_x = 1{\cdot}737$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7093 Å, $\mu = 1{\cdot}49$ mm^{-1}, $F(000) = 1022{\cdot}6$, $T = 297$ (3) K, $R = 0{\cdot}076$, $wR = 0{\cdot}068$ for 4042 observed reflections. There are two independent complex cations: an aqua and a perchlorato complex. The coordination geometry about Cu^{II} for both of these complexes is a distorted square pyramid with the diaminodiamide (*N*-Mebcen) equatorial and the O atom of H_2O or ClO_4^- axial. The two chiral amine N centres have the *RR* or *SS* configuration. In $[Cu(ClO_4)(N\text{-Mebcen})]^+$, the conformation of the quadridentate ligand, *N*-Mebcen, is the unstable form, with both terminal six-membered chelate rings in a twist form and with the central five-membered ring in a *gauche* form. On the other hand, in $[Cu(H_2O)(N\text{-Mebcen})]^{2+}$, one of the two six-membered rings adopts a twist form, and the other six- and five-membered chelate rings are of chair form and *gauche* form, respectively.

Introduction. Recently, we have initiated systematic studies on transition-metal complexes of diaminodiamides. Previously, we have reported the crystal structures of the copper(II) complexes of *N,N'*-bis(*β*-carbamoylethyl)ethylenediamine, bcen (Lee, Lu, Liu, Chung & Lee, 1984), *N,N'*-bis(*β*-carbamoylethyl)-*N,N'*-dimethylethylenediamine, *N*-Me_2bcen (Lu, Shan, Chao & Chung, 1987), *N,N'*-bis(*β*-carbamoylethyl)-2-hydroxytrimethylenediamine, bchtn (Lee, Hong, Liu, Chung & Lee, 1984), *N,N'*-bis(*β*-carbamoylethyl)trimethylenediamine, bctn (Hong, Lee, Lee, Chao & Chung, 1987). We now report the crystal structures of the aqua and the perchlorato copper(II) complexes of *N,N'*-bis(*β*-carbamoylethyl)-*N*-methylethylenediamine, *N*-

---

* 4-Methyl-4,7-diazadecanediamine.

† Department of Physics.

‡ Department of Chemistry.