mura et al.[29] support this: delocalization or withdrawal of electrons from the metal center makes it easier for a complex to accept additional electrons. For example, the Mo(VI) to Mo(V) reduction potential for the S-ligated, delocalized $MoO_2(Et_2dtc)_2$ is −0.83 V (Me_2SO)[30] while in the less delocalized O-ligated $MoO_2(ox)_2$ it is −1.07 V (Me_2SO).[31]

As might be expected, the complex is like a binuclear version of the diketonate $MoO_2(acac)_2$, which functions as an olefin epoxidation and an ethanol oxidation catalyst.[11-13] The catalytic properties of the triketonate complexes are under investigation to see if the binuclearity confers any advantage.

Acknowledgment. Support from NSF Grants CHE-8300516 and CHE-8609272 and a Faculty Research Grant from CSUS are gratefully acknowledged.

Supplementary Material Available: Tables listing magnetic moments, thermal parameters, bond lengths and angles associated with non-hydrogen atoms, and least-squares planes and a figure depicting a cyclic voltammogram (13 pages); a table of calculated and observed structure factors (16 pages). Ordering information is given on any current masthead page.

---

(29) Nakamura, A.; Nakayama, M.; Subihashi, K.; Otsuka, S. *Inorg. Chem.* **1979**, *18*, 394.

(30) DeHayes, L. J.; Faulkner, H. C.; Doub, W. H., Jr.; Sawyer, D. T. *Inorg. Chem.* **1975**, *14*, 2110.

(31) Isbell, A. F.; Sawyer, D. T. *Inorg. Chem.* **1971**, *10*, 2449.

Contribution from the Institute of Inorganic Chemistry,
University of Zürich, Winterthurerstrasse 190, 8057 Zürich, Switzerland

Synthesis and Structure of Dimeric Metal Complexes with N(3)/N(9)-Chelating Hypoxanthine Ligands and with Bridging Water Molecules: $[M_2(\mu\text{-hyxan})_2(SO_4)_2(\mu\text{-}H_2O)_2(H_2O)_2]$ (M = Cu, Cd, Zn; hyxan = Hypoxanthine)

Erich Dubler,* Gaby Hänggi, and Helmut Schmalle

Received August 4, 1989

Three new dimeric metal complexes of hypoxanthine (hyxan) with the general formula $M^{II}(hyxan)SO_4{\cdot}2H_2O$ with M = Cu, Zn, or Cd have been synthesized from acidic aqueous solutions. They all crystallize in the triclinic space group $P\bar{1}$ with two formula units per cell. The cell dimensions are a = 7.470 (2) Å, b = 8.529 (2) Å, c = 8.675 (2) Å, α = 77.32 (2)°, β = 87.70 (2)°, γ = 65.40 (2)°, and V = 489.5 (7) Å^3 for $Cu(hyxan)SO_4{\cdot}2H_2O$, a = 7.278 (2) Å, b = 8.714 (4) Å, c = 8.789 (8) Å, α = 102.45 (5)°, β = 91.46 (4)°, γ = 113.05 (3)°, and V = 497.1 (3) Å^3 for $Zn(hyxan)SO_4{\cdot}2H_2O$, and a = 7.343 (1) Å, b = 8.856 (1) Å, c = 9.002 (3) Å, α = 101.55 (2)°, β = 92.36 (3)°, γ = 112.86 (1)°, and V = 523.9 (4) Å^3 for $Cd(hyxan)SO_4{\cdot}2H_2O$. The structures of the copper and cadmium complexes were refined on the basis of 2809 and 6857 observed reflections to R values of 0.055 and 0.036, respectively. Single-crystal and powder X-ray data indicate that the zinc complex is virtually isostructural with its cadmium and copper analogues. The complexes exhibit a new dimeric structure type with molecular centrosymmetric units, $[M_2(\mu\text{-hyxan})_2(SO_4)_2(\mu\text{-}H_2O)_2(H_2O)_2]$. The two metal atoms are bridged by two N(3)/N(9)-chelating hypoxanthine ligands and by two water molecules. The metal–metal distances are 3.151 (1) Å (Cu) and 3.452 (1) Å (Cd). Distorted octahedral coordination of the metal atoms by two N and by four O atoms is observed with a pronounced (4 + 1 + 1) elongation of the octahedron in the copper complex. The bridging water molecules are stabilized by very strong hydrogen bonds of the type O–H···O with a minimum O···O distance of 2.57 Å. In the neutral hypoxanthine ligand, hydrogen atoms are attached at N(1) and N(7), which are involved in hydrogen bonds of the type N–H···O(sulfate). The purine rings are stacked, rotated 180° with respect to each other, with stacking distances of 3.34 and 3.30 Å, respectively. A review of X-ray structure determinations of metal–hypoxanthine complexes as well as of polynuclear copper and cadmium complexes with bridging water molecules is given.

Introduction

The stereochemistry of complexes formed between metal ions and nucleic acid bases, nucleosides, or nucleotides is believed to be important in determining the activity of many compounds of biological interest.[1,2]

The coordination properties of adenine and guanine, the major purine bases present in DNA and RNA, have been the subject of different crystallographic studies.[3,4] In contrast, only a few structures of metal complexes of the oxopurines hypoxanthine (hyxan), xanthine, uric acid, or allopurinol are available.

Hypoxanthine (1,7-dihydro-6*H*-purin-6-one) occasionally occurs as a constituent of the nucleoside inosine in minor amounts in transfer RNA.[5] It also is an intermediate product of purine metabolism, formed by enzymatical degradation of nucleic acids. The molybdenum- and iron-containing enzyme xanthine oxidase catalyzes the biological oxidation of hypoxanthine via xanthine to uric acid, which subsequently is released from the active site of the enzyme.[6] Defects in purine metabolism result in an increase of the uric acid level and in the deposition of sodium hydrogen urate monohydrate crystals in joints. This disease, known as gout, is clinically treated by the drug allopurinol (pyrazolo[3,4-*d*]pyrimidin-6-one), which also is a substrate for xanthine oxidase.[7] Alloxanthine (pyrazolo[3,4-*d*]pyrimidin-2,6-dione), the enzymatic oxidation product of allopurinol, is believed to remain bound to the reduced form of the molybdenum center of xanthine oxidase, thus inactivating the enzyme and inhibiting uric acid formation.[8]

Previous crystallographic investigations of metal complexes of unsubstituted hypoxanthine have elucidated three different coordination types. They are labeled I, IIb, and III in the coordination scheme given in Figure 1.

Type I represents monomeric complexes with monodentate coordination of hypoxanthine through the nitrogen atom N(7). In dimeric complexes of *type IIb*, two metal ions are bridged by four N(3)- and N(9)-chelating hypoxanthine ligands. *Type III* finally involves a polymeric complex, where hypoxanthine is coordinating through N(3) and N(7) to different metal ions, forming

---

* To whom correspondence should be addressed.

(1) Barton, J. K.; Lippard, S. J. In *Nucleic Acid Metal Interactions*; Spiro, T. G., Ed.; Metal Ions in Biology, Vol. 1; Wiley: New York, 1980; p 31.

(2) Marzilli, L. G.; Kistenmacher, T. G.; Eichhorn, G. L. In *Nucleic Acid-Metal Interactions*; Spiro, T. G., Ed.; Metal Ions in Biology, Vol. 1; Wiley: New York, 1980; p 179.

(3) Hodgson, D. J. *Prog. Inorg. Chem.* **1977**, *23*, 211.

(4) Sletten, E. G. *The Jerusalem Symposia on Quantum Chemistry and Biochemistry*; Jerusalem Academy of Sciences and Humanities: Jerusalem, 1977; Vol. 9, p 53.

(5) Hurst, D. T. In *An Introduction to the Chemistry and Biochemistry of Pyrimidines, Purines and Pteridines*; Wiley: New York, 1980; p 179.

(6) Stiefel, E. J. *Prog. Inorg. Chem.* **1977**, *22*, 1.

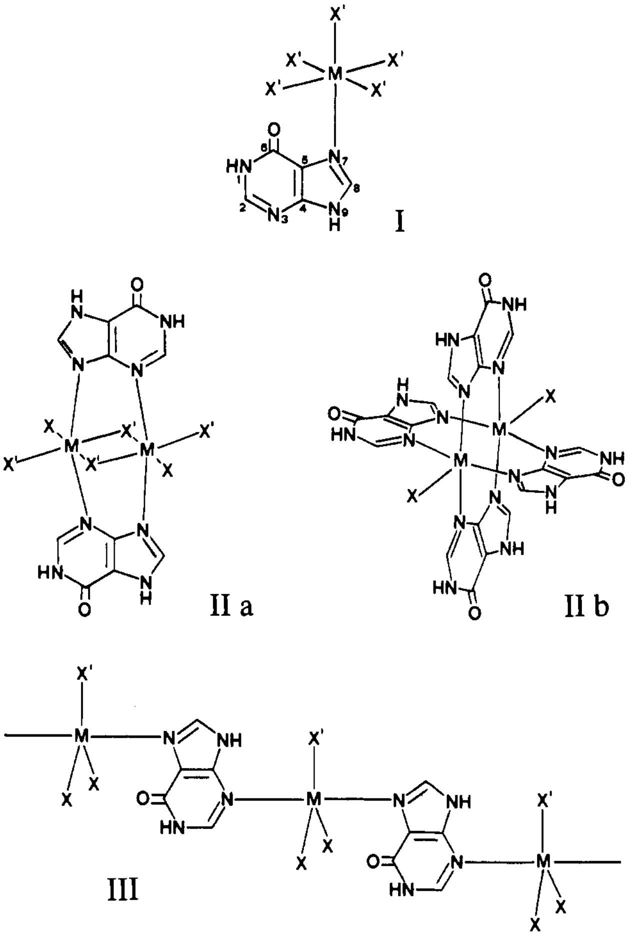
(7) Hille, R.; Massey, V. In *Nucleic Acid Metal Interactions*; Spiro, T. G., Ed.; Metals Ions in Biology, Vol. 7; Wiley: New York, 1985; p 443.

(8) Hawkes, T. R.; George G. N.; Bray, R. C. *Biochem. J.* **1984**, *218*, 961.

0020-1669/90/1329-2518$02.50/0 © 1990 American Chemical Society

Table I. Coordination and Protonation Sites of Hypoxanthine (hyxan), Established by X-ray Crystallography

compd	structure type (Figure 1)	coord	protonation	ref
hyxan			N(1), N(9)	9
$(hyxan^+)Cl \cdot H_2O$			N(1), N(7), N(9)	10
$(hyxan^+)NO_3 \cdot H_2O$			N(1), N(7), N(9)	11
$(hyxan^+)[AuCl_4] \cdot 2H_2O$	no coord		N(1), N(7), N(9)	12
$M^{II}(hyxan)SO_4 \cdot 5H_2O$ (M = Co, Ni)	I: $X' = H_2O$	N(7)	N(1), N(9)	13, 14
$Ru^{III}(hyxan)(NH_3)_5Cl_3 \cdot 3H_2O$	I: $X' = NH_3$	N(7)	N(1), N(9)	15
$M^{II}(hyxan)SO_4 \cdot 2H_2O$ (M = Cu, Zn, Cd)	IIa: $X = SO_4^{2-}$, $X' = H_2O$	N(3), N(9)	N(1), N(7)	this work
$Cu^{II}(hyxan)_2Cl_2 \cdot 3H_2O$	IIb: $X = Cl^-$	N(3), N(9)	N(1), N(7)	16
$Cu^{II}(hyxan)SO_4 \cdot H_2O$	III: $X = SO_4^{2-}$, $X' = H_2O$	N(3), N(7)	N(1), N(9)	13



I

II a

II b

III

Figure 1. Schematic presentation of the coordinating interaction of hypoxanthine with metal ions (M), established by X-ray crystallography.

infinite metal hypoxanthine chains.

Coordination and protonation sites of hypoxanthine and its metal complexes established by X-ray crystallography are summarized in Table I. In this context we report here synthesis and structure of complexes with the general formula $M^{II}(hyxan)SO_4 \cdot 2H_2O$ (M = Cu, Zn, Cd) with a new dimeric coordination type (IIa, Figure 1).

Table II. Analytical Data (%) of Metal Complexes of the Type $M(hyxan)SO_4 \cdot 2H_2O$[a]

compd	C	H	N	S	H_2O[b]
$CuC_5H_8N_4O_7S$	18.10	2.43	16.89	9.67	10.9
	18.10	2.34	16.67	9.70	11.0
$ZnC_5H_8N_4O_7S$	18.00	2.42	16.80	9.61	10.8
	18.09	2.55	16.58	9.81	10.8
$CdC_5H_8N_4O_7S$	15.78	2.12	14.72	8.42	9.5
	15.88	2.19	14.51	8.66	9.3

[a] The first value given is the calculated value, and the second value, the observed value. [b] The water content was derived from thermogravimetric analysis.

Table III. Crystal Data and Structure Determination Parameters of $M(hyxan)SO_4 \cdot 2H_2O$

	M = Cu	M = Zn	M = Cd
chem formula	$C_5H_8N_4O_7SCu$	$C_5H_8N_4O_7SZn$	$C_5H_8N_4O_7SCd$
fw	331.74	333.57	380.60
a, Å	7.470 (2)	7.278 (2)	7.343 (1)
b, Å	8.529 (2)	8.714 (4)	8.856 (1)
c, Å	8.675 (2)	8.789 (8)	9.002 (3)
α, deg	77.32 (2)	102.45 (5)	101.55 (2)
β, deg	87.70 (2)	91.46 (4)	92.36 (3)
γ, deg	65.40 (2)	113.05 (3)	112.86 (1)
V, Å^3	489.5 (7)	497.1 (3)	523.9 (4)
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Z	2	2	2
T, K	295	295	295
λ, Å	0.71073	0.71073	0.71073
ρ_{calcd}, g·cm^{-3}	2.25		2.41
ρ_{obs}, g·cm^{-3}	2.25		2.40
μ, cm^{-1}	23.75		22.61
transm coeff	0.796–0.867		0.562–0.651
$R(F_o)$	0.055		0.036
$R_w(F_o)$	0.036		0.037

Experimental Section

Synthesis. Hypoxanthine and the metal salts were obtained from Fluka, Buchs, Switzerland, and used without further purification.

$Cu(hyxan)SO_4 \cdot 2H_2O$ Dimer (Diaquabis(μ-aqua)bis(μ-hypoxanthine)-disulfatodicopper(II)). This complex was prepared by adding 0.6 g (2.4 mmol) of $CuSO_4 \cdot 5H_2O$ in 4.5 mL of H_2O to a solution of 140 mg (0.52 mmol) of inosine in 4.5 mL of 0.5 N H_2SO_4. The reaction mixture was carefully heated until complete solution was observed and then kept for crystallization at 40 °C. After 1 week, blue crystals of distorted hexagonal prismatic shape were isolated from the solution. This complex turned out to be not a copper inosine but a copper hypoxanthine complex. The nucleoside inosine had obviously decomposed to hypoxanthine and ribose in the course of the reaction. The reaction of hypoxanthine (instead of inosine) with an excess of $CuSO_4 \cdot 5H_2O$ in acid solution results in a monohydrated complex with the general formula $Cu(hyxan)SO_4 \cdot H_2O$. However, this complex has a structure type completely different from that of the dihydrate presented here.[13]

$Zn(hyxan)SO_4 \cdot 2H_2O$ Dimer (Diaquabis(μ-aqua)bis(μ-hypoxanthine)-disulfatodizinc(II)). This compound was synthesized by heating a solution of 140 mg (1.03 mmol) of hypoxanthine and 0.6 g (2.1 mmol) of $ZnSO_4 \cdot 7H_2O$ in 6 mL of 0.5 N H_2SO_4. The resulting solution was kept for crystallization at 75 °C. After 10 days, colorless distorted prismatic crystals were formed.

$Cd(hyxan)SO_4 \cdot 2H_2O$ Dimer (Diaquabis(μ-aqua)bis(μ-hypoxanthine)-disulfatodicadmium(II)). To 140 mg (1.03 mmol) of hypoxanthine desolved in 5 mL of 1 N H_2SO_4 was added a solution of 0.8 g (3.1 mmol) of $CdSO_4 \cdot {}^8/_3H_2O$ in 5 mL of H_2O. The reaction mixture was heated to boiling for 2 h and then kept for crystallization at 40 °C. One week later,

---

(9) Schmalle, H.; Hänggi, G.; Dubler, E. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1988**, *C44*, 732.

(10) Sletten, J.; Jensen, L. H. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1969**, *B25*, 1608.

(11) Rosenstein, R. D.; Oberding, M.; Hyde, J. R.; Zubieta, J.; Karlin, K. D.; Seeman, N. C. *Cryst. Struct. Commun.* **1982**, *11*, 1507. Schmalle, H.; Hänggi, G.; Dubler, E. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1990**, *C46*, 340.

(12) Caira, M. R.; Nassimbeni, L. R.; Rodgers, A. L. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1975**, *B31*, 1112.

(13) Dubler, E.; Hänggi, G.; Bensch, W. *J. Inorg. Biochem.* **1987**, *29*, 269.

(14) Dubler, E.; Hänggi, G.; Schmalle, H. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1987**, *C43*, 1872.

(15) Kastner, M. E.; Coffey, K. F.; Clark, M. J.; Edmonds, S. E.; Eriks, K. *J. Am. Chem. Soc.* **1981**, *103*, 5747.

(16) Sletten, E. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1970**, *B26*, 1609.

Table IV. Positional Parameters of Cu(hyxan)$SO_4\cdot 2H_2O^a$

atom	x	y	z	U_{eq}/U_{iso}, Å
Cu	0.31849 (7)	0.68429 (6)	0.94617 (5)	0.0174 (1)
S(1)	−0.1334 (1)	0.8188 (1)	0.7699 (1)	0.0165 (2)
O(11)	−0.3309 (3)	0.9484 (3)	0.8043 (2)	0.0235 (5)
O(12)	−0.1107 (3)	0.6382 (3)	0.8314 (2)	0.0263 (6)
O(13)	−0.1217 (4)	0.8529 (3)	0.5983 (3)	0.0413 (7)
O(14)	0.0176 (4)	0.8505 (3)	0.8437 (3)	0.0419 (9)
N(1)	0.4786 (4)	0.7863 (4)	0.4756 (3)	0.0239 (7)
C(2)	0.3914 (6)	0.7916 (5)	0.6129 (4)	0.0252 (9)
N(3)	0.4541 (4)	0.6623 (3)	0.7377 (3)	0.0216 (7)
C(4)	0.6218 (5)	0.5168 (4)	0.7119 (3)	0.0201 (7)
C(5)	0.7143 (6)	0.5038 (5)	0.5708 (4)	0.0281 (9)
C(6)	0.6495 (6)	0.6437 (5)	0.4398 (4)	0.0322 (10)
O(6)	0.7244 (4)	0.6494 (4)	0.3107 (3)	0.0432 (9)
N(7)	0.8747 (4)	0.3409 (4)	0.5948 (3)	0.0234 (7)
C(8)	0.8720 (5)	0.2641 (5)	0.7472 (4)	0.0251 (8)
N(9)	0.7225 (4)	0.3636 (3)	0.8210 (3)	0.0196 (6)
O(1)	0.6861 (4)	0.5446 (3)	1.0485 (2)	0.0205 (6)
O(2)	0.3419 (4)	0.9091 (3)	0.9354 (3)	0.0247 (6)
H(1)	0.415 (6)	0.887 (5)	0.394 (5)	0.04
H(2)	0.276 (6)	0.889 (5)	0.620 (5)	0.04
H(7)	0.949 (6)	0.296 (5)	0.517 (5)	0.04
H(8)	0.984 (6)	0.145 (5)	0.799 (4)	0.04
H(11)	0.703 (7)	0.569 (6)	1.109 (5)	0.04
H(12)	0.766 (6)	0.561 (5)	0.979 (5)	0.04
H(21)	0.454 (6)	0.911 (5)	0.898 (5)	0.04
H(22)	0.315 (7)	0.944 (6)	0.998 (5)	0.04

$^a U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a^*_i\cdot a^*_j\cdot a_i\cdot a_j$

Table V. Positional Parameters of Cd(hyxan)$SO_4\cdot 2H_2O^a$

atom	x	y	z	U_{eq}/U_{iso}, Å
Cd	0.00729 (2)	0.20078 (2)	0.05438 (1)	0.0204 (1)
S(1)	−0.31406 (6)	0.32771 (5)	0.23558 (5)	0.0181 (1)
O(11)	−0.3807 (2)	0.4573 (1)	0.2034 (1)	0.0312 (3)
O(12)	−0.4520 (2)	0.1589 (1)	0.1593 (2)	0.0381 (3)
O(13)	−0.2930 (4)	0.3480 (2)	0.4001 (1)	0.0622 (7)
O(14)	−0.1164 (3)	0.3654 (2)	0.1870 (3)	0.0642 (7)
N(1)	0.2676 (2)	0.2752 (2)	0.5390 (1)	0.0251 (3)
C(2)	0.1910 (3)	0.2802 (2)	0.4024 (2)	0.0259 (3)
N(3)	0.1320 (2)	0.1553 (1)	0.2804 (1)	0.0226 (2)
C(4)	0.1548 (2)	0.0142 (2)	0.3043 (1)	0.0201 (3)
C(5)	0.2287 (2)	0.0001 (2)	0.4426 (1)	0.0222 (3)
C(6)	0.2936 (2)	0.1366 (2)	0.5734 (1)	0.0241 (3)
O(6)	0.3659 (2)	0.1413 (2)	0.7010 (1)	0.0372 (4)
N(7)	0.2247 (2)	−0.1583 (2)	0.4203 (1)	0.0250 (3)
C(8)	0.1517 (3)	−0.2334 (2)	0.2737 (2)	0.0260 (3)
N(9)	0.1068 (2)	−0.1338 (1)	0.1990 (1)	0.0228 (2)
O(1)	0.2315 (2)	0.0725 (1)	−0.0382 (1)	0.0221 (2)
O(2)	0.2693 (2)	0.4530 (2)	0.0756 (2)	0.0304 (3)
H(1)	0.290 (4)	0.363 (3)	0.612 (3)	0.034 (7)
H(2)	0.182 (4)	0.386 (3)	0.393 (3)	0.022 (6)
H(7)	0.260 (5)	−0.193 (4)	0.487 (3)	0.042 (8)
H(8)	0.136 (4)	−0.349 (3)	0.229 (3)	0.028 (6)
H(11)	0.272 (4)	0.087 (4)	−0.114 (3)	0.035 (8)
H(12)	0.356 (4)	0.105 (4)	0.020 (3)	0.040 (8)
H(21)	0.304 (4)	0.474 (3)	−0.022 (3)	0.032 (7)
H(22)	0.359 (5)	0.466 (5)	0.102 (4)	0.059 (11)

$^a U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a^*_i\cdot a^*_j\cdot a_i\cdot a_j$

Table VI. Interatomic Bond Distances (Å) of M(hyxan)$SO_4\cdot 2H_2O$

	M = Cu	M = Cd		M = Cu	M = Cd
Metal Coordination Polyhedra					
M–N(3)	2.043 (3)	2.367 (2)	M–O(2)	1.978 (4)	2.278 (2)
M–N(9′)	2.008 (3)	2.274 (2)	M–O(14)	2.193 (3)	2.190 (3)
M–O(1)	2.599 (3)	2.426 (2)	M–M′	3.151 (1)	3.452 (1)
M–O(1′)	1.957 (4)	2.344 (1)			
Hypoxanthine					
N(1)–C(2)	1.335 (5)	1.347 (3)	C(5)–N(7)	1.385 (4)	1.366 (3)
C(2)–N(3)	1.302 (4)	1.311 (2)	N(7)–C(8)	1.344 (5)	1.336 (2)
N(3)–C(4)	1.401 (4)	1.380 (3)	C(8)–N(9)	1.331 (5)	1.335 (3)
C(4)–C(5)	1.384 (5)	1.386 (3)	N(9)–C(4)	1.366 (4)	1.363 (2)
C(5)–C(6)	1.385 (5)	1.418 (2)	C(6)–O(6)	1.233 (5)	1.231 (3)
C(6)–N(1)	1.431 (5)	1.404 (3)	N(3)–N(9)	2.467 (4)	2.449 (3)
Sulfate					
S(1)–O(11)	1.496 (2)	1.482 (1)	S(1)–O(13)	1.459 (3)	1.450 (2)
S(1)–O(12)	1.455 (3)	1.445 (1)	S(1)–O(14)	1.464 (4)	1.464 (2)

colorless crystals with distorted prismatic shape could be isolated. Analytical data of the three complexes are shown in Table II.

Crystallographic Studies. Cell parameters of all three complexes were obtained by least-squares refinement of 25 reflections in the interval 5° ≤ θ ≤ 15° carefully centered on an Enraf-Nonius CAD-4 diffractometer.

From the cell data given in Table III it is evident that the zinc and the cadmium complexes exhibit similar unit cells, whereas the reduced cell of the copper complex seems to be slightly different. The cell of the copper complex, however, can be transformed to a cell demonstrating a virtually isostructural relationship to the respective cells of the cadmium and zinc complexes, a = 7.470 (2) Å, b = 8.689 (2) Å, c = 8.675 (2) Å, α = 100.43 (2)°, β = 92.30 (2)°, γ = 116.81 (2)°, V = 489.5 (7) Å^3. Since this new cell does not respresent a reduced cell, we have choosen the reduced cell given in Table III (exhibiting the shortest possible cell vectors) for the structure refinement of the copper complex. The positional parameters of the copper complex given in Table IV may easily be transformed to show the close relationship with the data of the cadmium complex (Table V) by $x = (x + y) - 1$, $y = y - 0.5$, $z = 1 - z$.

Intensity data for the copper and the cadmium complexes were collected with graphite-monochromatized Mo Kα radiation. During the data collections, crystal stabilities were checked with six standard reflections measured every 2 (copper complex) or 3 (cadmium complex) h. For both complexes, no loss of intensity was observed. Five standard reflections were collected every 250 reflections (Cu) and six standard reflections every 300 reflections (Cd) to control orientation. The intensities were corrected for Lorentz and polarization effects, and a numerical absorption correction on the basis of six (Cu) or ten (Cd) crystal faces was applied.

Both structures were solved by Patterson syntheses using the program SHELXS86[17] and were refined with SHELX76.[18] The refinements of the structures were carried out by full-matrix least-squares calculations minimizing $\sum w(|F_o| - |F_c|)^2$, with $w = K/\sigma^2(F)$ (K_{Cu} = 1.48, K_{Cd} = 3.50). In both structures, all hydrogen atoms could be localized in the difference Fourier maps and were refined with variable positional parameters. For the copper compound, the thermal parameters of the hydrogen atoms were fixed at 0.04 Å^2, whereas for the cadmium compound isotropic thermal parameters were included in the least-squares refinements. The final refinements converged to R = 0.055, R_w = 0.036 for the copper complex and to R = 0.036, R_w = 0.037 for the cadmium analogue. The maximum and minimum heights of the final difference Fourier maps were 1.63 e·Å^{-3} located 0.88 Å from C(5) and −1.26 e·Å^{-3} located 0.39 Å from O(6) for the copper complex and 2.87 e·Å^{-3} (0.56 Å from Cd) and −2.50 e·Å^{-3} (0.23 Å from Cd) for the cadmium analogue.

Crystal parameters are summarized in Table III. Atomic parameters and equivalent isotropic thermal parameters are listed in Tables IV and V.

Discussion

Dimeric Molecular Structure. The structure of the copper as well as of the cadmium complex consists of molecular centrosymmetric dimeric units, $[M_2(\mu\text{-hyxan})_2(SO_4)_2(\mu\text{-}H_2O)_2(H_2O)_2]$. The two metal atoms are bridged by two N(3)/N(9)-chelating neutral hypoxanthine molecules and by two water molecules. The metal–metal distances are 3.151 (1) Å in the copper complex and 3.452 (1) Å in the cadmium complex. On the basis of very similar unit cells (Table III) as well as nearly coincident X-ray powder diffraction diagrams, the zinc complex is considered to be isostructural with its cadmium and copper analogues.

The dimeric complexes described here represent a new structure type for a hypoxanthine metal complex (type IIa in Figure 1). For the purine analogue adenine however, a similar structure has already been observed in the cadmium complex, $[Cd_2(\mu\text{-adeninium})_2(NO_3)_4(\mu\text{-}H_2O)_2](NO_3)_2$.[19] The configuration of the dimeric molecule is shown in Figure 2, and a stereoview of the unit cell is given in Figure 3. Interatomic bonding distances and

---

(17) Sheldrick, G. M. SHELXS86. In *Crystallographic Computing*; Sheldrick, G. M.; Krüger, C., Goddard, R., Eds.; Oxford University Press: Oxford, England, 1985; p 175.

(18) Sheldrick, G. M. *SHELX76. Program for Crystal Structure Determination*; University of Cambridge, England, 1976.

(19) Wei, C. H.; Jacobson, K. B. *Inorg. Chem.* **1981**, *20*, 356.

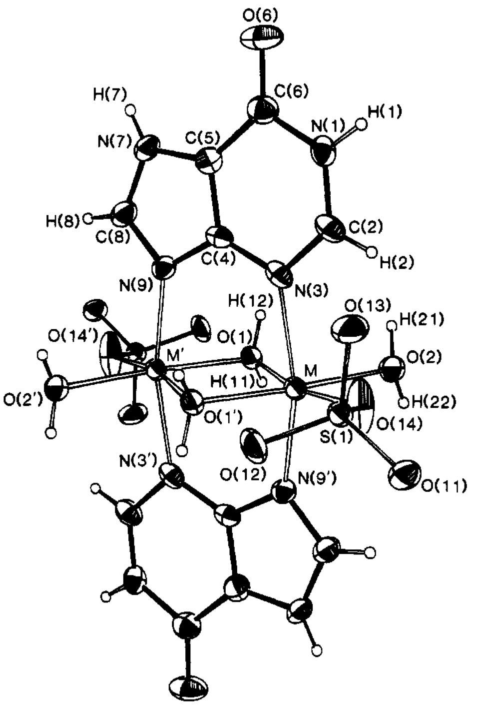


Figure 2. Structure of the dimeric units $[M_2(\mu\text{-hyxan})_2(SO_4)_2(\mu\text{-}H_2O)_2(H_2O)_2]$. The thermal ellipsoids shown refer to the copper complex and are drawn to the 50% probability level.

angles are summarized in Tables VI and VII, respectively.

Bridging of two metal atoms by N(3)/N(9)-chelating hypoxanthine molecules also occurs in $Cu(hyxan)_2Cl_2{\cdot}3H_2O$,[16] but in that complex, there are four bridging hypoxanthine ligands and no bridging water molecules. This bonding scheme (type IIb in Figure 1) leads to a Cu–Cu distance of 3.024 Å, which is significantly shorter than the corresponding distance of 3.151 Å found in the copper complex described here. The "bite" distance N(3)–N(9) of hypoxanthine, however, stays remarkably constant within the three dimeric hypoxanthine complexes characterized to date: 2.467 (4) Å in $Cu(hyxan)SO_4{\cdot}2H_2O$, 2.449 (3) Å in $Cd(hyxan)SO_4{\cdot}2H_2O$, and 2.463 and 2.438 Å respectively in $Cu(hyxan)_2Cl_2{\cdot}3H_2O$ (calculated according to the published coordinates in ref 16). In neutral noncoordinating hypoxanthine, N(9) but not N(7) is protonated and the N(3)–N(9) "bite" distances are 2.430 (2) and 2.429 (2) Å, respectively.[9]

Table VII. Interatomic Bond Angles (deg) of $M(hyxan)SO_4{\cdot}2H_2O$

	M = Cu	M = Cd
Metal Coordination Polyhedra		
N(3)–M–N(9′)	159.8 (1)	154.9 (1)
N(3)–M–O(1)	79.6 (1)	77.7 (1)
N(3)–M–O(1′)	87.1 (1)	81.9 (1)
N(3)–M–O(2)	89.9 (1)	93.2 (1)
N(3)–M–O(14)	97.2 (1)	91.3 (1)
N(9′)–M–O(1)	82.0 (1)	82.6 (1)
N(9′)–M–O(1′)	85.9 (1)	81.9 (1)
N(9′)–M–O(2)	96.1 (1)	100.8 (1)
N(9′)–M–O(14)	102.4 (1)	111.2 (1)
O(1)–M–O(1′)	93.7 (1)	87.3 (1)
O(1)–M–O(2)	83.2 (1)	86.3 (1)
O(1)–M–O(14)	168.5 (1)	162.9 (1)
O(1′)–M–O(2)	176.0 (1)	172.6 (1)
O(1′)–M–O(14)	97.1 (1)	104.3 (1)
O(2)–M–O(14)	85.8 (1)	81.3 (1)
Hypoxanthine		
C(6)–N(1)–C(2)	127.2 (3)	125.6 (2)
N(1)–C(2)–N(3)	123.5 (3)	124.6 (2)
C(2)–N(3)–C(4)	112.7 (3)	113.4 (2)
N(3)–C(4)–C(5)	125.8 (3)	124.7 (2)
C(4)–C(5)–C(6)	121.1 (3)	121.3 (2)
C(5)–C(6)–N(1)	109.7 (3)	110.3 (2)
C(4)–C(5)–N(7)	107.9 (3)	107.0 (1)
C(5)–N(7)–C(8)	104.8 (3)	106.2 (2)
N(7)–C(8)–N(9)	113.2 (3)	112.7 (2)
C(8)–N(9)–C(4)	106.0 (3)	105.3 (2)
N(9)–C(4)–C(5)	108.1 (3)	108.7 (2)
N(3)–C(4)–N(9)	126.1 (3)	126.5 (2)
C(6)–C(5)–N(7)	130.9 (4)	131.7 (2)
N(1)–C(6)–O(6)	123.6 (3)	122.1 (2)
C(5)–C(6)–O(6)	126.7 (4)	127.5 (2)
Metal–Hypoxanthine		
M–N(3)–C(2)	121.1 (2)	117.3 (2)
M–N(3)–C(4)	126.1 (2)	129.3 (1)
M–N(9′)–C(4′)	126.7 (2)	129.0 (2)
M–N(9′)–C(8′)	126.5 (2)	125.6 (1)
M–O(14)–S(1)	134.7 (2)	130.9 (1)
Sulfate		
O(11)–S(1)–O(12)	110.7 (2)	112.2 (1)
O(11)–S(1)–O(13)	107.1 (1)	107.1 (1)
O(11)–S(1)–O(14)	107.9 (2)	107.6 (1)
O(12)–S(1)–O(13)	110.2 (2)	110.9 (1)
O(12)–S(1)–O(14)	110.5 (2)	110.9 (1)
O(13)–S(1)–O(14)	110.4 (2)	107.9 (2)

Bridging Water Molecules. One interesting aspect of the dimeric structures described here is the bridging binding mode of the water molecule. Whereas the tendency to act as a bridging ligand between two metal atoms in polynuclear complexes is quite familiar for OH^- and O^{2-}, only a few examples are known involving a bridging H_2O molecule. The bonding characteristics of all such copper and cadmium complexes we are aware of, characterized

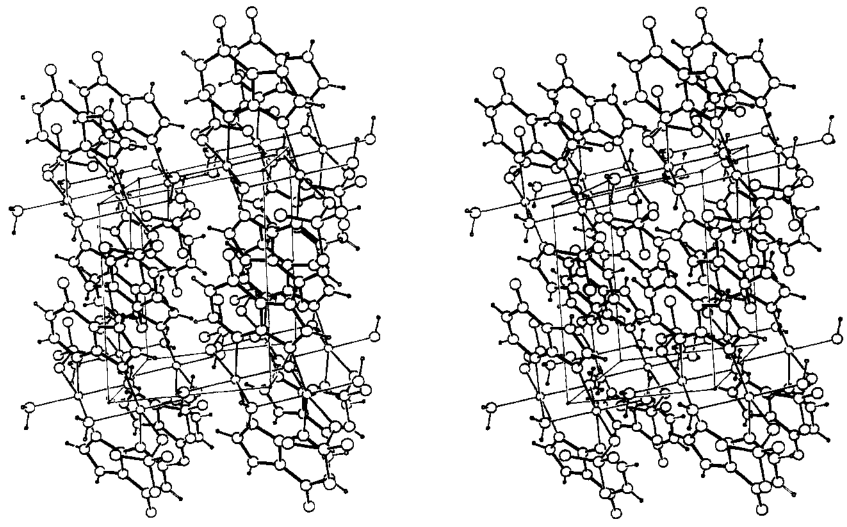


Figure 3. Stereoview of the unit cell of $M(hyxan)SO_4{\cdot}2H_2O$. The parameters drawn refer to the cadmium complex. Axis orientation: *a*, down; *b*, across; *c*, toward viewer.

Table VIII. Bonding Characteristics (Å, deg) of Bridging Water Molecules in Copper(II) and Cadmium(II) Complexes

polynuclear unit^{a}	M–M′	O–M	O–M′	M–O–M′	O(H$_1$)···O	O(H$_2$)···O	O–H$_1$–O	O–H$_2$–O	ref
$[Cu_2(\mu\text{-hyxan})_2(SO_4)_2(\mu\text{-}H_2O)_2(H_2O)_2]$	3.151 (1)	2.599 (3)	1.957 (4)	86.3 (1)	2.685 (5)	2.570 (4)	173 (6)	168 (4)	this work
$[Cu_2(\mu\text{-L})(\mu\text{-OH})(\mu\text{-}H_2O)]^{3+}$	3.145 (4)	2.519 (12)	2.519 (12)	77.3 (4)	3.01	3.01	*c*	*c*	21
$[Cu_2(\mu\text{-}Cl_3CCO_2)_2(Cl_3CCO_2)_2(\text{proxyl})_2\text{-}(\mu\text{-}H_2O)]$	3.529	1.994 (9)	2.351 (9)	108.4 (4)	2.549 (12)	2.559 (14)	*c*	*c*	22
$[Cu_2(\text{mep})_2(\text{mep}^-)_2(\mu\text{-}H_2O)]^{2+}$	3.893 (2)^{d}	2.339 (6)	2.358 (4)	112.0 (2)	2.639 (8)	2.636 (9)	177	139	23
$[Cu_4(\mu\text{-dithoox}^{2-})_2(SO_4)(\mu\text{-}H_2O)_2\text{-}(H_2O)_2]$	4.304 (2)^{d}	2.300 (3)	2.487 (3)	128.0	2.720^{b}	2.773 (5)	169^{b}	176^{b}	24
$[Cu(\text{bzim})_2(HCOO)_2(\mu\text{-}H_2O)]_n$	5.200^{b,d}	2.625 (2)	2.625 (2)	164.2 (5)	*c*	*c*	*c*	*c*	25
$[Cd_2(\mu\text{-hyxan})_2(SO_4)_2(\mu\text{-}H_2O)_2(H_2O)_2]$	3.452 (1)	2.426 (2)	2.344 (1)	92.7 (1)	2.675 (2)	2.623 (3)	174 (4)	167 (3)	this work
$[Cd_2(\mu\text{-ad}^+)_2(NO_3)_4(\mu\text{-}H_2O)_2]^{2+}$	3.616 (2)	2.397 (5)	2.467 (7)	96.0 (2)	2.81 (1)	2.99 (1)	139 (10)	163 (13)	19
$[Cd_4(\mu\text{-phdta}^{4-})_2(\mu\text{-}H_2O)_2(H_2O)_6]$	4.189^{b,e}	2.379 (5)	2.619 (8)	113.8^{b}	*c*	*c*	*c*	*c*	26

[a] Abbreviation of ligand names: hyxan, hypoxanthine; mep, 2-amino-2-methyl-1-propanol; proxyl, 2,2,4,4-tetramethylpyrrolinyl-1-oxy; bzim, benzimidazole; L, 20-membered macrocyclic tetraimine ligand; dithioox, *N,N′*-bis(2-hydroxyethyl)dithiooxamide; phdta, *o*-phenylenediamine-*N,N,N′,N′*-tetraacetic acid; ad, adenine. [b] Values not given in the original reference paper but calculated on the basis of published atomic coordinates. [c] Hydrogen atom positions and/or hydrogen-bonding contacts not established. [d] Intramolecular distance between two Cu atoms bridged by one H_2O molecule only. [e] Intramolecular distance between two Cd atoms bridged by two H_2O molecules only.

Table IX. Hydrogen-Bonding Contacts (Å, deg) in $M(\text{hyxan})SO_4\cdot 2H_2O$

	M = Cu			M = Cd		
X–H···Y	X–H	X–Y	X–H···Y	X–H	X–Y	X–H···Y
N(1)–H(1)···O(11)	0.94 (3)	2.821 (4)	165 (4)	0.86 (3)	2.791 (2)	167 (3)
N(1)–H(1)···O(13)	0.94 (3)	3.071 (4)	128 (3)	0.86 (3)	3.201 (3)	130 (3)
N(7)–H(7)··O(13)	0.90 (4)	2.715 (4)	164 (3)	0.80 (3)	2.713 (3)	161 (2)
O(1)–H(11)···O(6)	0.64 (4)	2.685 (5)	173 (6)	0.77 (3)	2.675 (2)	174 (4)
O(1)–H(12)···O(12)	0.86 (5)	2.570 (4)	168 (4)	0.94 (3)	2.623 (3)	167 (3)
O(2)–H(21)···O(11)	0.89 (5)	2.770 (5)	172 (3)	0.96 (3)	2.841 (3)	173 (3)
O(2)–H(22)···O(11)	0.66 (5)	2.773 (4)	160 (6)	0.65 (4)	2.756 (3)	167 (4)

by X-ray crystallography, are summarized in Table VIII. In addition, a μ-aqua–μ-oxo bridging of two copper centers has been postulated from infrared and from X-ray data for $[LCu(\mu\text{-}H_2O)\text{–}(\mu\text{-}O)CuL](ClO_4)_2$ with L = 1,4,7-trimethyl-1,4,7-triazacyclononane.[20]

From the data listed in Table VIII it seems evident that the stability of μ-aqua complexes is enhanced by strong hydrogen bonding of the water molecules to oxygen atoms of other bridging or nonbridging ligands. In both complexes described here, the bridging water oxygen atom O(1) is involved in short hydrogen-bonded contacts of 2.570 (4) Å (Cu) and 2.623 (3) Å (Cd) to the sulfate oxygen atom O(12) and of 2.635 (5) Å (Cu) and 2.675 (2) Å (Cd) to the hypoxanthine oxygen atom O(6). The hydrogen-bonded O···O contact of 2.57 Å found in the copper complex represents an extremely strong hydrogen bond, since the minimum O···O distance found in O–H···O bonds of water molecules is 2.55 Å.[27,28] The geometry about the bridging water oxygen atom O(1) is distorted tetrahedral with bond angles M–O(1)–M′ = 86.3 (1)° (Cu) and 92.7 (1)° (Cd) and O(12)···O(1)···O(6) = 109.7 (2)° (Cu) and 106.2 (1)° (Cd).

It is also interesting to note that the bonding angle M–O–M′ at the bridging water molecules, listed in Table VIII, is not restricted to values corresponding to an approximate tetrahedral environment of the oxygen atom but is varying from about 77 to 164°. Therefore, the resulting metal-to-metal distances, M–M′, also show great differences.

Environment of Copper and Cadmium. The dimeric units contain two edge-sharing MN_2O_4 octahedra, M being coordinated by N(3) and N(9) of two different hypoxanthine molecules, by two bridging and one nonbridging water oxygen atoms, and by one sulfate oxygen atom. The coordination octahedra are distorted with bonding angles ranging from 79.6 (1) to 102.4 (1)° in the copper complex and from 77.7 (1) to 111.2 (1)° in the cadmium complex. In addition, Jahn–Teller distortion results in a (4 + 1 + 1)-elongated coordination octahedron of the copper complex, with O(14) (2.193 (3) Å) and O(1) (2.599 (3) Å) occupying the apical positions. The metal ions are displaced −0.06 Å toward the nitrogen atom N(9′) (Cu) and 0.16 Å toward the nitrogen atom N(3) (Cd) from the best plane defined by O(1)–O(1′)–O(2)–O(14). The plane through the four coordinating nitrogen atoms is nearly perpendicular to the plane defined by M–O(1)–M′–O(1′). The corresponding interplanar angles are 88.7° (Cu) and 88.2° (Cd), respectively.

Geometry of the Hypoxanthine Molecule. In neutral hypoxanthine, hydrogen atoms are attached at N(1) and N(9),[9] but coordination occurs exclusively through N(7) in its monomeric complexes. In the dimeric hypoxanthine complexes described here, hydrogen atoms are attached at N(1) and N(7) of the neutral ligand, and chelating coordination occurs through N(3) and N(9). We have demonstrated in two recent papers[29,14] that metal coordination at a nitrogen atom in oxopurines induces changes in the geometry of the purine moiety similar to, but smaller than, those induced by protonation at the respective nitrogen atom. The major effect of nitrogen *protonation* in oxopurines is to widen the corresponding C–N–C angle by about 3–4°,[30] whereas nitrogen *coordination* also increases this angle but only by about 0.5°. In the dimeric complexes presented here, this effect is demonstrated by the bonding angle C(2)–N(3)–C(4), which is increased by coordination at N(3) from a mean value of 112.1 (1)° in neutral hypoxanthine, where no hydrogen atom is attached at N(3), to 112.7 (3)° (Cu) and to 113.4 (2)° (Cd). In contrast, the bonding angle C(4)–N(9)–C(8) is decreased by coordination instead of protonation from a mean value of 106.8 (1)° in neutral hypoxanthine, where a hydrogen atom is attached to N(9), to 106.0 (3)° (Cu) and to 105.3 (2)° (Cd). In both complexes, the coordinating purine rings show small but significant deviations from planarity. Maximum deviations of an individual atom from the least-squares planes through the nine ring atoms are 0.028 Å

---

(20) Chaudhuri, P.; Ventur, D.; Wieghardt, K.; Peters, E.-M.; Peters, K.; Simon, A. *Angew. Chem.* **1985**, *97*, 55.
(21) Drew, M. G. B.; Nelson, J.; Esho, F.; McKee, V.; Nelson, S. M. *J. Chem. Soc., Dalton Trans.* **1982**, 1837.
(22) Porter, L. C.; Doedens, R. J. *Inorg. Chem.* **1985**, *24*, 1006.
(23) Muhonen, H. *Inorg. Chem.* **1986**, *25*, 4692.
(24) Chauvel, C.; Girerd, J. J.; Jeannin, Y.; Kahn, O.; Lavigne, G. *Inorg. Chem.* **1979**, *18*, 3015.
(25) Bukowska-Strzyzewska, M.; Tosik, A. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1983**, *C39*, 203.
(26) Nakasuka, N.; Azuma, S.; Tanaka, M. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1986**, *C42*, 1736.
(27) Lutz, H. D. *Struct. Bonding* **1988**, *69*, 98.
(28) Ferraris, G.; Ivaldi, G. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1988**, *B44*, 341.
(29) Hänggi, G.; Schmalle, H.; Dubler, E. *Inorg. Chem.* **1988**, *27*, 3131.
(30) Taylor, R.; Kennard, O. *J. Mol. Struct.* **1982**, *78*, 1.

Inorg. Chem. **1990**, *29*, 2523-2527 **2523**

(C(5)) in Cu(hyxan)$SO_4 \cdot 2H_2O$ and 0.011 Å (N(7)) in the respective cadmium compound. The extraannular oxygen atom O(6) lies 0.050 Å below (Cu) or 0.029 Å above (Cd) this purine plane.

Purine Stacking and Hydrogen Bonding. A packing diagram of the structure of M(hyxan)$SO_4 \cdot 2H_2O$ is presented in Figure 3. On the basis of the classification proposed by Bugg,[31] a solid-state stacking pattern of the purine rings of type II occurs, where the stacking bases are rotated approximately 180° with respect to each other. In M(hyxan)$SO_4 \cdot 2H_2O$, the stacking base pairs are related by a center of inversion and therefore are exactly parallel by crystallographic symmetry. The stacking involves interactions of the polar carbonyl groups with the imidazole rings of adjacent purines, but there is only minor direct overlap because the rings are not perpendicular in relation to their translation axis. The stacking distances between hypoxanthine bases, calculated as the mean distance of all atoms of one molecule from the least-squares plane through the stacking molecule is 3.30 Å in Cu(hyxan)$SO_4 \cdot 2H_2O$ and 3.34 Å in Cd(hyxan)$SO_4 \cdot 2H_2O$.

A summary of hydrogen-bonded contacts and their geometry is presented in Table IX. The coordinating hypoxanthine molecules are involved in three hydrogen bonds of the type N–H···O with a bifurcated hydrogen-bonding system around H(1). As mentioned above, the bridging water molecule is involved in strong hydrogen bonds with a minimum O···O donor–acceptor distance of 2.57 Å (Cu) and 2.62 Å (Cd), respectively. The nonbridging water molecule exhibits hydrogen bonds with corresponding minimum O···O distances of 2.77 Å (Cu) and 2.76 Å (Cd), respectively.

Acknowledgment. We thank Professor H. R. Oswald for standing support of this project. Research grants from the Swiss National Science Foundation (No. 2.838-085) are gratefully acknowledged.

Supplementary Material Available: Tables listing details of data collection and structure refinement, anisotropic thermal parameters, and bonding distances and angles involving H atoms for the two structures (4 pages); listings of observed and calculated structure factors (32 pages). Ordering information is given in any current masthead page.

---

(31) Bugg, C. E. *The Jerusalem Symposia on Quantum Chemistry and Biochemistry*; Jerusalem Academy of Sciences and Humanities: Jerusalem, 1972; Vol 4., p 178.

Contribution from the Chemistry Department,
The Ohio State University, Columbus, Ohio 43210

Synthesis and Structural Characterization of a Neutral Lacunar Complex Formed by Deprotonation of Methyl Groups of the Cyclidene Macrocycle

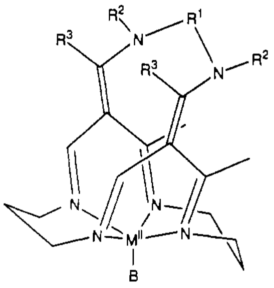
Kenneth A. Goldsby, Alan J. Jircitano, Dennis L. Nosco, James C. Stevens, and Daryle H. Busch*

Received July 7, 1989

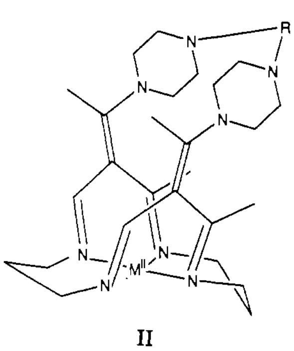
X-ray structural analysis, electrochemistry, and reactivity with dioxygen are reported for the complex [Co{$(CH_2)_2(MeN)_2(CH_2)_6$[16]cyclidene}]. The neutral complex is formed by deprotonation of the parent $(CH_2)_6$-bridged lacunar cyclidene complex. The structural differences between the parent and deprotonated complexes can be understood in terms of the redistribution of electron density upon deprotonation. The centralization of electron density and reduction in charge concomitant with deprotonation result in a large cathodic shift for the potential required to oxidize the cobalt(II) and structurally analogous nickel(II) complexes. The neutral cobalt(II) complex autoxidizes much faster than the corresponding cationic parent complex, and this has prevented dioxygen affinity measurements. [CO{$(CH_2)_2(MeN)_2(CH_2)_6$[16]cyclidene}] crystallized in the monoclinic system ($P2_1/n$) with unit cell dimensions a = 13.824 (2) Å, b = 11.351 (2) Å, c = 17.852 (2) Å, β = 115.16 (1)°, and Z = 4; R = 0.064 and R_w = 0.073 for 2666 observed reflections.

Introduction

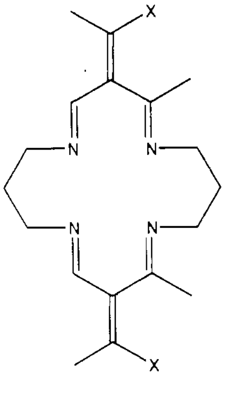
A major focus of our work has involved the design and synthesis of a new family of lacunar (structure I) and vaulted (structure II) complexes capable of binding small molecules and/or organic substrates.[1,2] These complexes are based on the parent cyclidene macrocycle shown in structure III. The cyclidene macrocycle is particularly amenable to these studies, since the ligand superstructure may be easily modified to control the shape and size of the substrate binding site.[1-5]



I



II



(X = OR, NRR^1)

III

In the course of developing the synthetic methodology used to modify the cyclidene macrocycle, we have explored the depro-

---

* To whom correspondence should be addressed at the Chemistry Department, The University of Kansas, Lawrence, KS 66045-0046.

(1) (a) Cairns, C. J.; Busch, D. H. *Progress in Macrocycle Chemistry*; Izatt, R. N., Christensen, J. J., Eds.; Wiley-Interscience: New York, 1987; pp 1-51. (b) Busch, D. H. *Oxygen Complexes and Oxygen Activation*; Martell, A. E., Sawyer, D. T., Eds.; Plenum Publ. Co.: New York, 1988; pp 61-85.

0020-1669/90/1329-2523$02.50/0