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Facile CO₂ Uptake by Zinc(II)–Tetraazacycloalkane Complexes. 2. X-ray Structural Studies of (μ -Monomethyl carbonato)(1,4,8,11-tetraazacyclotetradecane)zinc(II) Perchlorate, Zn(O₂COCH₃)([14]aneN₄)(ClO₄), Bis(μ -monomethyl carbonato)tris[(1,4,8,12-tetraazacyclopentadecane)zinc(II)] Perchlorate, [[Zn([15]aneN₄)]₃(O₂COCH₃)₂](ClO₄)₄, and (Monomethyl carbonato)(1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane)zinc(II) Perchlorate, [Zn(O₂COCH₃)(Me₄[14]aneN₄)](ClO₄)

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Received February 13, 1984

X-ray structures of the three titled (monomethyl carbonato)zinc(II) complexes, Zn(O₂COCH₃)(C₁₀H₂₄N₄)(ClO₄) (1), [[Zn(C₁₁H₂₆N₄)]₃(O₂COCH₃)₂](ClO₄)₄ (2), and [Zn(O₂COCH₃)(C₁₄H₃₂N₄)](ClO₄) (3), that are obtained from reaction of Zn(II)–tetraazacycloalkane complexes with CO₂ in methanol, have been determined (C₁₀H₂₄N₄ = [14]aneN₄, C₁₁H₂₆N₄ = [15]aneN₄, C₁₄H₃₂N₄ = Me₄[14]aneN₄). Crystal data: for 1, monoclinic, space group *P*2₁/*n*, *a* = 12.128 (2) Å, *b* = 15.509 (1) Å, *c* = 9.793 (1) Å, β = 95.36 (1)°, *V* = 1833.9(4) Å³, *Z* = 4; for 2, monoclinic, space group *C*2/*c*, *a* = 37.189 (5) Å, *b* = 9.714 (1) Å, *c* = 16.749 (2) Å, β = 100.80 (1)°, *V* = 5943 (1) Å³, *Z* = 4; for 3, triclinic, space group *P* $\bar{1}$, *a* = 11.462 (1) Å, *b* = 12.324 (2) Å, *c* = 8.369 (1) Å, α = 109.04 (1)°, β = 98.51 (2)°, γ = 87.52 (1)°, *V* = 1105.2 (3) Å³, *Z* = 2. In 1, Zn²⁺ is surrounded pseudooctahedrally by [14]aneN₄ in a planar fashion and by monomethyl carbonate oxygens occupying the axial positions. The monomethyl carbonate plays a role of a bridging ligand, linking two neighboring [Zn([14]aneN₄)]²⁺ units to give a linear chain structure along the *a* axis. Compound 2 is a trimer of [Zn([15]aneN₄)]²⁺ bridged by monomethyl carbonate. A central Zn is in six-coordination, with four nitrogens of [15]aneN₄ occupying the in-plane positions, whereas two terminal Zn atoms are in five-coordination of the trigonal-bipyramidal type. Compound 3 is a mononuclear five-coordinate complex of the trigonal-bipyramidal type. Monomethyl carbonate in 3 is coordinated to Zn²⁺ unidentately. Coordination stereochemistries about Zn have been discussed in connection with the efficient CO₂ fixation by the present Zn(II) complexes.

Introduction

In the preceding paper, we reported the preparation and characterization of a series of (monoalkyl carbonato) zinc(II) complexes, which are obtained from the reaction of four-coordinate Zn(II) complexes with tetraazacycloalkanes with CO₂ in alcohol.¹ Particularly fascinating characteristics of the present system are that CO₂ is taken up under mild conditions and is fixed very easily into the Zn complex as monoalkyl carbonate. Furthermore, some of the Zn complexes were found to undergo a reversible CO₂ absorption–desorption reaction. The chemistries of the Zn(II) complexes described in the preceding paper suggest that ligation of tetraazacycloalkane gives rise to active reaction sites effective for the CO₂ fixation. Data of IR and ¹³C NMR spectra indicate that there are two different types of coordination modes for ligation of monoalkyl carbonate. In this study, single-crystal X-ray analyses of the three titled compounds, Zn(O₂COCH₃)([14]aneN₄)(ClO₄) (1), [[Zn([15]aneN₄)]₃(O₂COCH₃)₂](ClO₄)₄ (2), and [Zn(O₂COCH₃)(Me₄[14]aneN₄)](ClO₄) (3), have been carried out, with the aim of determination of the coordination stereochemistries and investigation of structural factors upon efficient CO₂ fixation.

Experimental Section

Materials. The preparation of the compounds has been described in the preceding paper.¹ When a MeOH–H₂O mixed solution (ca. 4:1 (v/v)) of Zn([14]aneN₄)(ClO₄)₂ was allowed to stand in a refrigerator for several days, CO₂ was spontaneously taken up to give colorless plates of 1. Compound 2, which contains Zn([15]aneN₄)²⁺ and CH₃OCO₂[–] in a composition of 3:2, crystallized as colorless columnar crystals from a methanol solution of the crude 1:1 complex, Zn([15]aneN₄)(O₂COCH₃)(ClO₄) (2'), at –20 °C. Colorless block crystals of 3 were obtained by recrystallization from methanol under a CO₂ atmosphere.

Collection and Reduction of X-ray Diffraction Data. Diffraction data were obtained on a Rigaku AFC-5 four-circle diffractometer with use of graphite-monochromatized Mo K α radiation. Although the *a* axis of

2 was as long as 37.189 (5) Å, Mo K α radiation was used successfully because of the systematic absence (*hkl* for *h* + *k* = 2*n*). Diffraction data were measured at room temperature for 1 and 3 but at 123 K for complex 2, because it is known that complexes having the [15]aneN₄ ligand often involve structural disorder as to chelate ring conformations in the crystal structures.² The low-temperature measurements were made with an attached Rigaku variable-temperature apparatus using a cold nitrogen gas stream method. The procedures used for data collection as well as methods used in the solution and refinement of the structures were standard and have been described previously.³ Absorption corrections were applied with a numerical integration procedure with a Gaussian grid (6 × 6 × 6). Pertinent crystallographic parameters for the three compounds are summarized in Table I.

Solution and Refinement of the Structures. For complex 1, both of the two crystallographically independent Zn atoms were located initially at the center of symmetry. As the refinement proceeded, however, it turned out that a thermal ellipsoid of Zn(1) became extraordinarily elongated along the normal to a plane formed by four nitrogens (hereafter abbreviated as N₄ plane) of the [14]aneN₄ ligand and its equivalent isotropic temperature factor became about twice as large as that of Zn(2). The situation was similar to those reported for structural analyses of [Zn(NCS)₂([14]aneN₄)]⁴ and [Zn(H₂O)(TPP)]⁵ (TPP = tetraphenylporphine), structures of which were refined by taking disorder concerning an out-of-plane displacement of the Zn atom into consideration. Thus, the structure of 1 was solved in a similar way with the Zn(1) atom in two disordered positions (Zn(1) and Zn(1')), equidistantly above and below the N₄ plane with an occupancy factor of 0.5 each. The Zn(1) and Zn(1') atoms are related by inversion at the crystallographic center of symmetry. Calculations of the refinements in this manner converged nicely to give a reasonable structure with the normal thermal parameters for the Zn(1) atom.

The structure of 2 was solved under the crystallographic requirement that the Zn(1) atom was located at a center of symmetry, although the Zn(1)([15]aneN₄) moiety should not have such a symmetry. It was assumed that a gauche five-membered and a skew six-membered ring in

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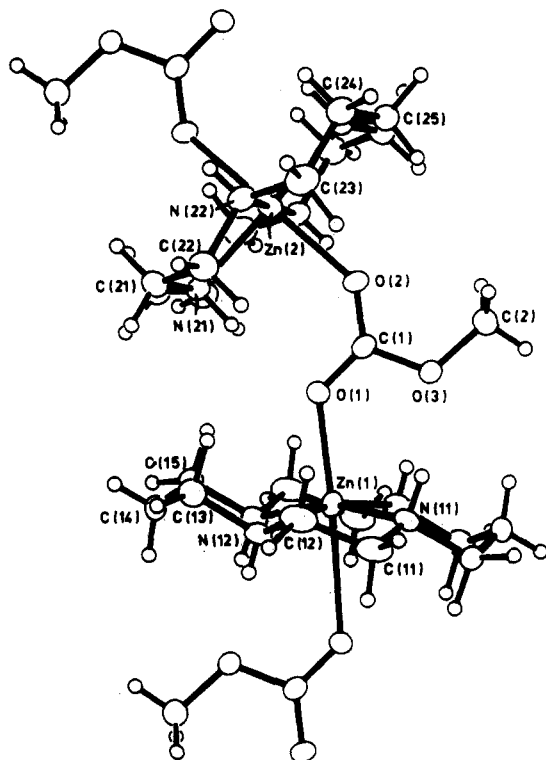


Figure 1. Perspective view of the structure of $\text{Zn}(\text{O}_2\text{COCH}_3)([14]\text{aneN}_4)^+$ in **1**. Thermal ellipsoids are depicted at the 30% probability level. The disordered $\text{Zn}(1')$ atom is omitted for clarity.

the $\text{Zn}(1)([15]\text{aneN}_4)$ moiety are randomly interchanged with occupancy factors of 0.5. Such disorder is often found in the crystal structures of metal complexes containing $[15]\text{aneN}_4$ and has been solved in the same way (*vide infra*).² For the sake of the disorder, the occupancy factors of C(11) and C(12) were assumed to be 1, whereas that of C(16) was taken to be 0.5 (see Figure 2).

Calculations of the structure analysis of **3** converged smoothly.

In each structure, non-hydrogen and hydrogen atoms were refined anisotropically and isotropically, respectively. For **1** and **3**, all the hydrogen atoms were located by difference syntheses, but for **2**, five hydrogen atoms out of 42 were found and included in the calculations. The final *R* indices are listed in Table I. Positional and thermal parameters for non-hydrogen atoms in compounds **1**–**3** are given in Tables II–IV, respectively.

All the calculations were carried out on the HITAC M-200H computer at the Computer Center of the Institute for Molecular Science with the Universal crystallographic computation program system UNICS III.⁶

Results and Discussion

Figures 1–3 show perspective views of complexes **1**–**3**, respectively. Table V lists relevant bond distances and angles.

$\text{Zn}(\text{O}_2\text{COCH}_3)([14]\text{aneN}_4)(\text{ClO}_4)$ (1**).** There are two crystallographically independent Zn atoms in the unit cell. Each Zn atom is surrounded pseudooctahedrally by four nitrogens of the $[14]\text{aneN}_4$ ligand in a plane and by two oxygens of monomethyl carbonate ligands occupying the axial positions. The $[14]\text{aneN}_4$ ligands bound to Zn(1) and Zn(2) adopt the same overall stereochemistry with the most stable chelate ring conformations. The monomethyl carbonate ion plays a role of bridging ligand, linking Zn(1) and Zn(2) and forming a linear chain structure. Although both the Zn(1) and Zn(2) atoms are surrounded by the same ligands, their coordination geometries are different (Figure 4). Zn(1) is disordered above and below the N_4 plane and is displaced by 0.272 (4) Å from it. As a result, the Zn(1)–O(1) (or Zn(1')–O(1')) bond distance (2.143 (3) Å) is normal, but Zn(1)–O(1') (or Zn(1')–O(1)) lengthens up to 2.685 (3) Å. Thus, Zn(1) is more or less five-coordinate. On the other hand, Zn(2) is situated at a crystallographic inversion center and thus resides precisely in the N_4 plane to form a tetragonal six-coordinate

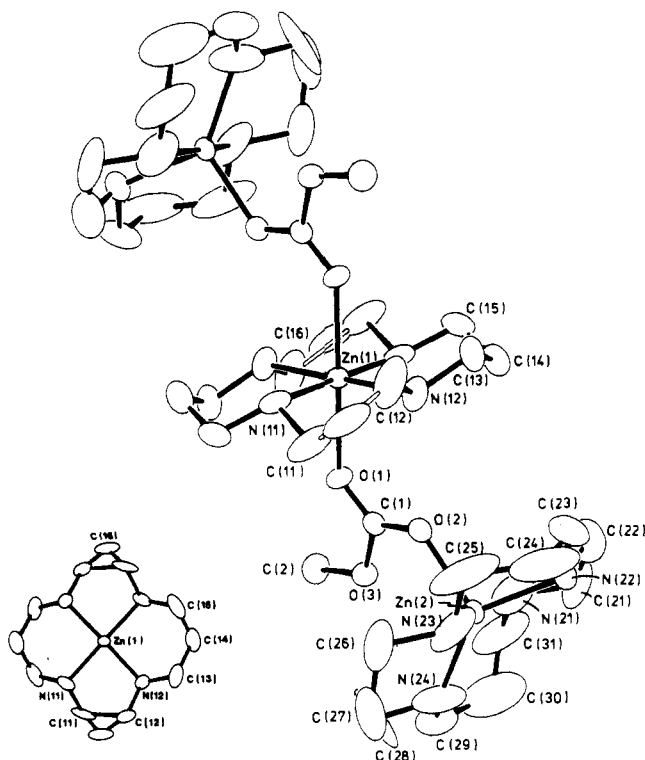


Figure 2. Perspective view of the structure of $[\text{Zn}([15]\text{aneN}_4)_3(\text{O}_2\text{COCH}_3)_2]^{4+}$ in **2**. Thermal ellipsoids are depicted at the 30% probability level. A chelate ring composed of Zn(1), N(11), C(11), C(16), C(12), and N(12) is disordered in five-membered $[\text{Zn}(1)\text{--N}(11)\text{--C}(11)\text{--C}(12)\text{--N}(12)]$ and six-membered $[\text{Zn}(1)\text{--N}(11)\text{--C}(11)\text{--C}(16)\text{--C}(12)\text{--N}(12)]$ rings with an occupancy factor of 0.5 each (see text). Inset shows the disordered structure about Zn(1) viewed along the axial bonds.

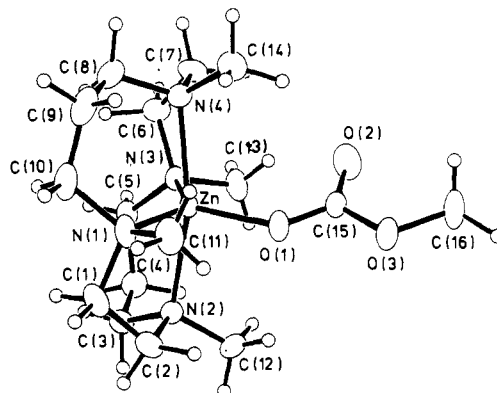


Figure 3. Perspective view of the structure of $[\text{Zn}(\text{O}_2\text{COCH}_3)(\text{Me}_4[14]\text{aneN}_4)]^+$ in **3**. Thermal ellipsoids are depicted at the 30% probability level.

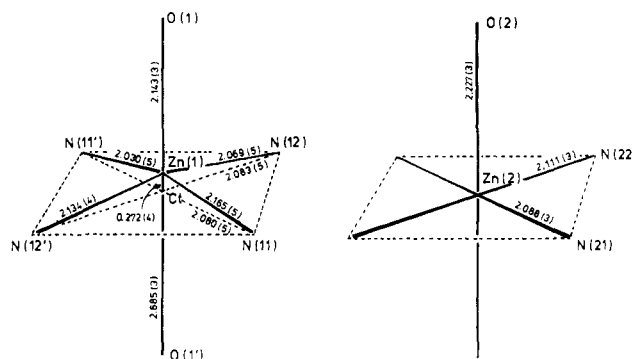


Figure 4. Coordination geometries about the Zn(1) (A) and Zn(2) (B) atoms in $\text{Zn}(\text{O}_2\text{COCH}_3)([14]\text{aneN}_4)(\text{ClO}_4)$ (**1**). The disordered $\text{Zn}(1')$ atom is omitted for clarity.

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Table I. Crystallographic Parameters

	1	2 ^a	3
formula	ZnClO ₇ N ₄ C ₁₂ H ₂₇	Zn ₃ Cl ₄ O ₂₂ N ₁₂ C ₃₇ H ₈₄	ZnClO ₇ N ₄ C ₁₆ H ₃₅
fw	440.21	1387.11	496.31
cryst syst	monoclinic	monoclinic	triclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> , Å	12.128 (2)	37.189 (5)	11.462 (1)
<i>b</i> , Å	15.509 (1)	9.714 (1)	12.324 (2)
<i>c</i> , Å	9.793 (1)	16.749 (2)	8.369 (1)
α , deg	90	90	109.04 (1)
β , deg	95.36 (1)	100.80 (1)	98.51 (2)
γ , deg	90	90	87.52 (1)
<i>V</i> , Å ³	1833.9 (4)	5943 (1)	1105.2 (3)
<i>Z</i>	4	4	2
<i>d</i> _{calcd} , g cm ⁻³	1.59	1.55	1.491
<i>d</i> _{measd} , g cm ⁻³	1.58	1.52	1.490
cryst size, mm	0.50 × 0.30 × 0.08	0.36 × 0.32 × 0.16	0.52 × 0.62 × 0.36
scan range	1.1 + 0.5 tan θ	1.2 + 0.5 tan θ	1.4 + 0.5 tan θ
μ , mm ⁻¹	1.568	1.449	1.31
2 θ range, deg	2–60	2–55	2–55
no. of unique data ^b	2610	3231	4776
no. of variables	344	382	403
<i>R</i>	0.047	0.083	0.045
<i>R</i> _w	0.052	0.102	0.061

^a Diffraction data were measured at 123 K. Unit cell parameters at 293 K are *a* = 37.595 (6) Å, *b* = 9.808 (2) Å, *c* = 16.927 (3) Å, β = 100.45 (1)°, *V* = 6138 (2) Å³, and *d*_{calcd} = 1.50 g cm⁻³. ^b |*F*₀| > 3 σ (|*F*₀|).

Table II. Atomic Parameters for Zn(O₂COCH₃)([14]aneN₄)(ClO₄) (1)^a

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Zn(1) ^b	221 (1)	48 (2)	86 (3)	422 (13)	341 (8)	307 (7)	62 (14)	77 (11)	11 (6)
Zn(2)	5000	0	0	352 (3)	369 (3)	387 (3)	-8 (3)	-41 (3)	28 (4)
N(11)	157 (3)	-1197 (2)	-918 (4)	306 (18)	510 (22)	488 (21)	0 (16)	-71 (15)	-147 (18)
N(12)	130 (3)	-683 (2)	1839 (3)	300 (18)	546 (22)	402 (19)	-85 (16)	-5 (14)	73 (18)
C(11)	561 (4)	-1783 (3)	194 (5)	388 (25)	362 (25)	858 (36)	24 (21)	-106 (23)	-23 (25)
C(12)	-16 (4)	-1601 (3)	1455 (5)	435 (27)	522 (29)	732 (34)	-73 (23)	-69 (24)	169 (27)
C(13)	-598 (4)	-388 (3)	2849 (5)	475 (29)	887 (37)	376 (24)	-164 (26)	50 (21)	66 (26)
C(14)	-443 (4)	554 (4)	3207 (4)	398 (27)	1235 (48)	372 (25)	-119 (29)	86 (21)	-274 (30)
C(15)	-844 (4)	1180 (3)	2088 (5)	347 (23)	719 (33)	601 (29)	-1 (22)	52 (21)	-397 (26)
N(21)	6168 (3)	419 (2)	1561 (3)	293 (18)	461 (20)	374 (18)	23 (15)	46 (14)	-56 (16)
N(22)	4996 (3)	-1153 (2)	1146 (4)	364 (19)	437 (21)	474 (20)	39 (16)	80 (16)	68 (17)
C(21)	6105 (4)	-193 (3)	2702 (4)	410 (24)	630 (32)	369 (22)	26 (21)	-55 (19)	51 (21)
C(22)	5985 (4)	-1097 (3)	2123 (4)	496 (27)	557 (29)	450 (25)	99 (22)	-15 (21)	178 (22)
C(23)	4890 (4)	-1953 (3)	319 (5)	524 (29)	330 (24)	781 (36)	58 (21)	105 (25)	30 (23)
C(24)	3880 (4)	-1935 (3)	-725 (5)	453 (26)	384 (25)	646 (30)	-26 (20)	102 (23)	-90 (23)
C(25)	3923 (3)	-1337 (3)	-1949 (5)	409 (25)	497 (27)	515 (27)	-43 (21)	89 (20)	-141 (22)
O(1)	1988 (2)	150 (2)	172 (3)	319 (14)	561 (20)	383 (15)	-33 (13)	18 (11)	-105 (14)
O(2)	3662 (2)	505 (2)	1190 (3)	272 (15)	553 (19)	499 (17)	37 (13)	62 (12)	-86 (15)
O(3)	2132 (2)	689 (2)	2257 (3)	327 (15)	666 (20)	394 (16)	0 (14)	57 (12)	-118 (15)
C(1)	2637 (3)	434 (2)	1137 (4)	351 (22)	317 (22)	416 (23)	74 (17)	84 (18)	-1 (19)
C(2)	2826 (4)	1036 (4)	3385 (5)	470 (28)	1030 (44)	496 (28)	10 (29)	20 (23)	-239 (29)
Cl	2937 (1)	-1651 (1)	-6093 (1)	464 (6)	642 (7)	459 (6)	41 (6)	44 (5)	54 (6)
O(4)	3966 (3)	-1262 (3)	-5622 (4)	705 (27)	1206 (37)	1019 (33)	-226 (25)	-130 (23)	36 (29)
O(5)	2801 (4)	-1629 (4)	-7511 (5)	1055 (39)	2840 (73)	612 (26)	-712 (46)	150 (26)	-169 (40)
O(6)	2087 (4)	-1161 (4)	-5661 (6)	974 (38)	1927 (59)	1578 (50)	558 (39)	409 (35)	-148 (44)
O(7)	2878 (5)	-2454 (4)	-5534 (7)	1310 (45)	984 (39)	2274 (64)	-244 (34)	-473 (43)	657 (42)

^a Positional and thermal parameters are multiplied by 10⁴. ^b Occupancy factor of 0.5 (see text).

complex. A Zn(2)–O(2) distance of 2.227 (3) Å seems to be slightly longer than the normal value (vide infra). The difference in the coordination geometries about Zn(1) and Zn(2) arises from the bridge coordination of CH₃OCO₂⁻. Because CH₃OCO₂⁻ has an unsymmetrical molecular structure, two N₄ planes associated with Zn(1) and Zn(2) are not parallel and are at the angle of 45.5 (1)°. Therefore, steric constraints occur between the neighboring [14]aneN₄ macrocycles (H1(C15)···H(N21) = 2.24 (5) Å, H1(C15)···H1(C25) = 2.57 (6) Å, H1(C13)···H2(C21) = 2.63 (6) Å). On the other hand, the O(3) atom of the monomethyl carbonate ligand is located close to the Zn(1)([14]aneN₄) moiety and has a weak bonding interaction with H(N11) (2.39 (4) Å) to fix the structure. Consequently, the O(1) atom cannot approach the axial coordination site of Zn(1)([14]aneN₄) close enough to make a Zn–O bond with normal distance, in spite of the fact that separation of donor oxygens of the monomethyl carbonate from N₄ plane is larger for O(1) (2.412 (3) Å) than for O(2) (2.227

(3) Å). As a result, Zn(1) is required to assume the out-of-plane position. Five- or six-coordinate Zn complexes with four nitrogens in a plane often take an out-of-plane Zn structure.^{4,5} The amount of displacement from the N₄ plane spans a relatively wide range depending on the systems, and concomitantly so do the apical coordination bond lengths. Ab initio MO calculations for a hypothetical complex, *trans*-[ZnCl₂(NH₃)₄], show that the electronic potential surface is very flat with respect to the out-of-plane displacement of Zn.⁷

[[Zn([15]aneN₄)₃(O₂COCH₃)₂](ClO₄)₄] (2). Compound 2 was found to be a trimer of Zn([15]aneN₄) bridged by CH₃OCO₂⁻ (Figure 2). It was obtained as columns by slow recrystallization of the 1:1 complex (2') from methanol. Complex 2' is supposed to have a linear chain structure like 1. In the stage of crystal

Table III. Atomic Parameters for $[[\text{Zn}([15]\text{aneN}_4)]_3(\text{O}_2\text{COCH}_3)_2](\text{ClO}_4)_4 (2)^a$

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zn(1)	2500	2500	5000	348 (8)	290 (8)	398 (8)	19 (8)	107 (6)	-21 (8)
Zn(2)	953 (1)	2357 (1)	4590 (1)	453 (7)	548 (8)	350 (6)	-37 (6)	51 (5)	91 (6)
Cl(1)	1739 (1)	1467 (3)	8145 (2)	514 (16)	476 (15)	593 (17)	134 (14)	144 (13)	115 (14)
Cl(2)	130 (1)	3445 (3)	1029 (2)	412 (15)	652 (19)	832 (21)	-160 (15)	166 (14)	-68 (17)
O(1)	2037 (2)	1357 (7)	5347 (4)	307 (36)	444 (40)	599 (46)	-7 (32)	82 (32)	-9 (36)
O(2)	1509 (2)	2364 (6)	4801 (4)	473 (39)	356 (37)	400 (36)	14 (33)	107 (29)	-37 (32)
O(3)	1501 (2)	364 (7)	5416 (4)	477 (44)	519 (44)	565 (46)	-110 (36)	85 (36)	108 (37)
O(4)	1737 (3)	507 (19)	8673 (12)	1028 (96)	3213 (202)	4134 (241)	1055 (118)	1340 (130)	3076 (199)
O(5)	1528 (4)	2537 (12)	8212 (10)	1401 (114)	1068 (95)	2627 (162)	782 (85)	-214 (106)	-456 (99)
O(6)	2098 (3)	1695 (16)	8187 (13)	785 (86)	1748 (134)	4761 (290)	198 (94)	840 (129)	1562 (173)
O(7)	1608 (7)	857 (27)	7503 (10)	4314 (324)	4614 (351)	1585 (151)	2648 (285)	-679 (171)	-1724 (197)
O(8)	71 (3)	2196 (10)	1411 (6)	1241 (87)	877 (71)	1261 (87)	-323 (63)	605 (72)	166 (63)
O(9)	73 (5)	4500 (15)	1499 (10)	3246 (218)	1340 (115)	2801 (193)	-589 (132)	2006 (177)	-1104 (126)
O(10)	471 (3)	3564 (11)	853 (7)	777 (68)	1253 (90)	1811 (110)	16 (65)	658 (72)	433 (85)
O(11)	-128 (4)	3495 (16)	323 (12)	1787 (149)	1858 (152)	3318 (228)	-930 (128)	-1388 (149)	933 (158)
N(11)	2555 (2)	3747 (9)	6080 (5)	377 (50)	631 (62)	663 (61)	-132 (44)	194 (44)	-320 (51)
N(12)	2140 (3)	4075 (9)	4412 (6)	703 (67)	411 (53)	678 (66)	96 (49)	-125 (52)	1 (49)
N(21)	921 (3)	569 (15)	3728 (8)	806 (91)	1478 (126)	1406 (119)	207 (87)	-55 (82)	-694 (103)
N(22)	821 (3)	3339 (15)	3460 (6)	670 (73)	1997 (140)	641 (73)	447 (87)	188 (59)	648 (87)
N(23)	925 (3)	4227 (13)	5203 (8)	655 (75)	1228 (103)	1521 (120)	391 (74)	-120 (74)	-867 (94)
N(24)	650 (3)	1257 (14)	5286 (11)	851 (95)	1075 (109)	3227 (218)	362 (84)	1004 (122)	1096 (129)
C(1)	1698 (3)	1408 (10)	5173 (6)	487 (61)	357 (54)	376 (56)	-44 (49)	113 (46)	-37 (48)
C(2)	1711 (3)	-794 (12)	5817 (8)	721 (87)	461 (70)	1008 (102)	-26 (64)	107 (75)	433 (71)
C(11)	2225 (3)	4652 (14)	6000 (10)	511 (80)	899 (104)	1618 (145)	4 (73)	200 (86)	-912 (104)
C(12)	2246 (4)	5420 (14)	4884 (10)	1226 (132)	526 (86)	1357 (137)	436 (87)	-512 (104)	-325 (87)
C(13)	2155 (4)	4335 (15)	3566 (8)	850 (101)	926 (103)	803 (94)	-206 (84)	-175 (77)	549 (83)
C(14)	2081 (4)	2978 (14)	3047 (7)	919 (101)	961 (100)	579 (80)	-499 (85)	96 (72)	121 (74)
C(15)	2387 (4)	1982 (16)	3130 (7)	739 (86)	1431 (131)	566 (80)	-574 (91)	311 (67)	-237 (81)
C(16) ^b	2810 (6)	-702 (24)	4335 (20)	455 (149)	409 (141)	1881 (318)	-9 (117)	228 (173)	-420 (173)
C(21)	752 (5)	980 (26)	2924 (9)	1127 (138)	2976 (288)	580 (99)	587 (159)	-308 (93)	-762 (141)
C(22)	917 (6)	2483 (29)	2830 (9)	1585 (183)	3801 (405)	493 (96)	-58 (215)	133 (105)	-289 (165)
C(23)	1012 (5)	4665 (22)	3425 (12)	1122 (138)	2210 (215)	1814 (190)	187 (143)	703 (132)	1561 (176)
C(24)	925 (5)	5580 (19)	4045 (19)	1284 (165)	997 (143)	4837 (413)	398 (128)	1810 (224)	956 (208)
C(25)	1144 (4)	5386 (15)	5029 (16)	847 (121)	439 (89)	3995 (335)	-58 (86)	647 (166)	-229 (146)
C(26)	1082 (5)	3929 (22)	6142 (9)	1407 (155)	2269 (215)	810 (112)	1181 (156)	-236 (103)	-716 (130)
C(27)	791 (6)	2908 (27)	6448 (10)	1810 (202)	3150 (299)	558 (98)	1346 (206)	200 (111)	-2 (144)
C(28)	761 (8)	1389 (25)	6188 (10)	3629 (343)	2481 (257)	654 (111)	1593 (250)	1140 (164)	972 (145)
C(29)	561 (4)	-80 (16)	5257 (11)	853 (112)	914 (112)	1700 (167)	27 (90)	345 (109)	744 (114)
C(30)	475 (6)	-516 (20)	4392 (20)	1136 (171)	838 (140)	5057 (472)	-141 (128)	710 (229)	151 (221)
C(31)	765 (5)	-605 (21)	3873 (16)	757 (123)	1264 (161)	3186 (299)	-301 (118)	-68 (153)	-592 (187)

^a Positional and thermal parameters are multiplied by 10^4 . ^b Occupancy factor of 0.5 (see text).

Table IV. Atomic Parameters for $[\text{Zn}(\text{O}_2\text{COCH}_3)(\text{Me}_4[14]\text{aneN}_4)](\text{ClO}_4) (3)^a$

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zn	20541 (3)	24252 (4)	4856 (3)	294 (1)	338 (2)	354 (2)	47 (1)	117 (1)	131 (1)
Cl	6044 (1)	2065 (1)	-2618 (1)	522 (5)	432 (4)	601 (5)	17 (4)	137 (4)	219 (4)
O(1)	837 (2)	2373 (2)	1884 (3)	424 (13)	723 (18)	613 (16)	116 (12)	265 (12)	252 (14)
O(2)	-410 (3)	3794 (3)	1768 (4)	699 (19)	794 (21)	1047 (24)	209 (16)	347 (17)	527 (19)
O(3)	-638 (2)	2651 (2)	3294 (3)	517 (15)	763 (19)	654 (17)	90 (13)	314 (13)	308 (14)
O(4)	6554 (4)	2561 (4)	-881 (5)	1257 (33)	1245 (33)	729 (23)	-35 (26)	-98 (22)	395 (22)
O(5)	6119 (5)	2819 (4)	-3514 (6)	2070 (50)	1175 (34)	1225 (34)	-726 (34)	-562 (34)	900 (30)
O(6)	6642 (5)	1075 (4)	-3325 (6)	2208 (55)	1126 (35)	1351 (39)	865 (36)	1014 (39)	516 (29)
O(7)	4878 (4)	1790 (5)	-2673 (7)	804 (28)	1829 (51)	1673 (46)	-433 (30)	277 (30)	377 (38)
N(1)	2595 (2)	665 (2)	-250 (4)	414 (15)	358 (14)	660 (18)	40 (11)	260 (13)	166 (13)
N(2)	3495 (2)	2624 (2)	2679 (3)	362 (13)	577 (17)	423 (14)	19 (12)	96 (11)	247 (13)
N(3)	2572 (2)	3996 (2)	240 (3)	362 (13)	318 (12)	414 (13)	16 (10)	118 (10)	123 (10)
N(4)	983 (2)	2195 (3)	-2043 (3)	403 (14)	576 (18)	360 (13)	-45 (12)	31 (11)	126 (12)
C(1)	3716 (3)	629 (3)	869 (6)	455 (19)	491 (20)	899 (29)	157 (16)	224 (19)	375 (20)
C(2)	3680 (3)	1433 (4)	2673 (5)	446 (19)	742 (26)	708 (25)	107 (18)	101 (17)	479 (22)
C(3)	4630 (3)	3107 (3)	2522 (4)	341 (16)	700 (24)	487 (19)	-12 (15)	26 (14)	232 (17)
C(4)	4512 (3)	4267 (3)	2249 (5)	419 (18)	626 (23)	531 (21)	-140 (16)	55 (15)	149 (17)
C(5)	3868 (3)	4243 (3)	546 (4)	382 (16)	463 (18)	520 (19)	-24 (14)	157 (14)	171 (15)
C(6)	2136 (3)	3951 (3)	-1531 (5)	548 (21)	535 (21)	513 (19)	-6 (16)	42 (16)	325 (17)
C(7)	936 (3)	3387 (4)	-2126 (5)	509 (21)	721 (26)	551 (21)	60 (18)	-41 (17)	350 (20)
C(8)	1545 (4)	1394 (4)	-3486 (5)	556 (22)	874 (30)	389 (18)	-120 (21)	98 (16)	95 (19)
C(9)	1810 (4)	213 (4)	-3402 (5)	777 (28)	575 (24)	539 (23)	-166 (21)	279 (21)	-157 (18)
C(10)	2807 (4)	151 (3)	-2070 (5)	687 (25)	405 (19)	663 (24)	97 (17)	348 (20)	44 (17)
C(11)	1691 (4)	-29 (3)	79 (6)	578 (23)	434 (20)	867 (29)	-25 (17)	265 (21)	251 (19)
C(12)	3128 (3)	3304 (4)	4350 (4)	590 (23)	874 (30)	356 (18)	44 (20)	108 (16)	216 (18)
C(13)	1975 (3)	4957 (3)	1418 (5)	505 (20)	400 (18)	716 (24)	83 (15)	245 (18)	99 (17)
C(14)	-249 (3)	1820 (4)	-2176 (5)	407 (20)	887 (31)	605 (24)	-161 (20)	-1 (17)	162 (22)
C(15)	-47 (3)	2982 (3)	2263 (4)	360 (16)	501 (19)	405 (16)	15 (13)	127 (13)	115 (14)
C(16)	-1694 (4)	3283 (4)	3730 (6)	634 (27)	926 (34)	915 (33)	236 (24)	511 (25)	308 (27)

^a Positional and thermal parameters are multiplied by 10^4 except for positional parameter of Zn, for which the values are multiplied by 10^5 .

Table V. Relevant Bond Distances (Å) and Angles (deg)

Zn(O ₂ COCH ₃) ₂ ([14]aneN ₄)(ClO ₄) (1)			
Zn(1)-O(1)	2.143 (3)	Zn(2)-N(21)	2.088 (3)
Zn(1)-N(11)	2.165 (5)	Zn(2)-N(22)	2.111 (3)
Zn(1)-N(12)	2.069 (5)	O(1)-C(1)	1.252 (5)
Zn(1)-O(1')	2.685 (3)	O(2)-C(1)	1.243 (5)
Zn(1)-N(11')	2.030 (5)	O(3)-C(1)	1.363 (5)
Zn(1)-N(12')	2.134 (4)	O(3)-C(2)	1.430 (6)
Zn(2)-O(2)	2.227 (3)		
O(1)-Zn(1)-N(11)	94.4 (2)	O(2)-Zn(2)-N(21)	89.1 (1)
O(1)-Zn(1)-N(12)	98.0 (2)	O(2)-Zn(2)-N(22)	89.0 (1)
O(1)-Zn(1)-N(11')	100.5 (2)	N(21)-Zn(2)-N(22)	84.8 (1)
O(1)-Zn(1)-N(12')	96.7 (2)	N(21)-Zn(2)-O(2')	90.9 (1)
N(11)-Zn(1)-N(12)	83.4 (2)	N(21)-Zn(2)-N(22')	95.2 (1)
N(11)-Zn(1)-O(1')	82.1 (1)	N(22)-Zn(2)-O(2')	91.0 (1)
N(11)-Zn(1)-N(12')	90.9 (2)	Zn(1)-O(1)-C(1)	127.7 (3)
N(12)-Zn(1)-O(1')	83.4 (1)	Zn(2)-O(2)-C(1)	136.1 (3)
N(12)-Zn(1)-N(11')	96.7 (2)	C(1)-O(3)-C(2)	117.0 (3)
O(1')-Zn(1)-N(11')	83.0 (1)	O(1)-C(1)-O(2)	128.2 (4)
O(1')-Zn(1)-N(12')	81.6 (1)	O(1)-C(1)-O(3)	114.2 (3)
N(11')-Zn(1)-N(12')	85.1 (2)	O(2)-C(1)-O(3)	117.6 (3)
[[Zn([15]aneN ₄) ₂ (O ₂ COCH ₃) ₂](ClO ₄) ₄ (2)			
Zn(1)-O(1)	2.213 (7)	Zn(2)-N(23)	2.101 (13)
Zn(1)-N(11)	2.155 (9)	Zn(2)-N(24)	2.067 (17)
Zn(1)-N(12)	2.147 (9)	O(1)-C(1)	1.235 (11)
Zn(2)-O(2)	2.034 (6)	O(2)-C(1)	1.261 (11)
Zn(2)-N(21)	2.257 (15)	O(3)-C(1)	1.360 (12)
Zn(2)-N(22)	2.093 (12)	O(3)-C(2)	1.470 (13)
O(1)-Zn(1)-N(11)	89.0 (3)	N(22)-Zn(2)-N(23)	91.3 (5)
O(1)-Zn(1)-N(12)	91.7 (3)	N(22)-Zn(2)-N(24)	133.4 (5)
N(11)-Zn(1)-N(12)	93.6 (3)	N(23)-Zn(2)-N(24)	95.2 (6)
O(2)-Zn(2)-N(21)	92.5 (4)	Zn(1)-O(1)-C(1)	136.4 (6)
O(2)-Zn(2)-N(22)	102.3 (4)	Zn(2)-O(2)-C(1)	122.8 (6)
O(2)-Zn(2)-N(23)	93.1 (4)	C(1)-O(3)-C(2)	116.2 (8)
O(2)-Zn(2)-N(24)	123.3 (4)	O(1)-C(1)-O(2)	126.6 (9)
N(21)-Zn(2)-N(22)	77.3 (6)	O(1)-C(1)-O(3)	118.8 (8)
N(21)-Zn(2)-N(23)	169.0 (5)	O(2)-C(1)-O(3)	114.6 (8)
N(21)-Zn(2)-N(24)	89.7 (6)		
[Zn(O ₂ COCH ₃)(Me ₄ [14]aneN ₄)](ClO ₄) (3)			
Zn-O(1)	1.965 (3)	O(1)-C(15)	1.251 (4)
Zn-N(1)	2.143 (3)	O(2)-C(15)	1.237 (5)
Zn-N(2)	2.236 (3)	O(3)-C(15)	1.341 (5)
Zn-N(3)	2.130 (3)	O(3)-C(16)	1.438 (5)
Zn-N(4)	2.222 (3)		
O(1)-Zn-N(1)	100.1 (1)	N(2)-Zn-N(4)	166.2 (1)
O(1)-Zn-N(2)	92.0 (1)	N(3)-Zn-N(4)	83.8 (1)
O(1)-Zn-N(3)	121.7 (1)	Zn-O(1)-C(15)	132.4 (3)
O(1)-Zn-N(4)	101.7 (1)	C(15)-O(3)-C(16)	115.7 (4)
N(1)-Zn-N(2)	83.5 (1)	O(1)-C(15)-O(2)	127.3 (4)
N(1)-Zn-N(3)	138.0 (1)	O(1)-C(15)-O(3)	112.5 (3)
N(1)-Zn-N(4)	92.5 (1)	O(2)-C(15)-O(3)	120.1 (3)
N(2)-Zn-N(3)	90.4 (1)		

growth of **2**, monomethyl carbonates are partly lost. This is not strange in view of the fact that Zn²⁺ often prefers five-coordination and that the [15]aneN₄ macrocycle is bulkier than [14]aneN₄ and thereby bridge coordination of CH₃OCO₂⁻ is susceptible to steric hindrance (note that, even in the structure of **1**, the Zn(1)-O(1') distance (2.685 (3) Å) is substantially longer than a normal Zn-O bond length).⁸ As depicted in Figure 2, Zn(1) in the central segment resides at a crystallographic center of symmetry and takes coordination geometry of the tetragonally distorted octahedral type. On the other hand, two terminal Zn atoms, which are related by inversion at Zn(1), are in five-coordination. A chain structure formed by bridge coordination of monomethyl carbonate is very similar to that found for **1**. The overall stereochemistry of the [15]aneN₄ ligand in the central segment is of the same type as found in the crystal structure of [NiCl₂([15]aneN₄)].² The three six-membered and one five-membered chelate rings are in the chair, skew, chair, and gauche conformations. The skew six-membered and gauche five-membered chelate rings are statistically

disordered, i.e., randomly interchanged with each other in the crystal structure. Disorder of this type has been also found in the structures of [NiCl₂([15]aneN₄)] and [Ni(NCS)₂([15]aneN₄)] and is likely characteristic of [15]aneN₄ complexes.² Because of the disorder, the temperature factors of the atoms in the [15]aneN₄ macrocycle are fairly large. The coordination geometry of Zn(2) in the terminal segment is trigonal bipyramidal. Its trigonal plane is formed with O(2), N(22), and N(24). The axial bonds, Zn(2)-N(21) and Zn(2)-N(23), are longer than the in-plane bonds, giving an elongated hexahedron. In the terminal unit, the [15]aneN₄ is folded and each chelate ring is highly distorted. The distortion occurs in such a way that the steric hindrance from the O(3) atom of the monomethyl carbonate ligand is relieved. Rather large thermal ellipsoids for atoms in the terminal macrocyclic ligands are likely indicative of low rigidity of the conformational structure. The Zn(2)-O(2) bond distance of 2.034 (6) Å is within the normal range, whereas the Zn(1)-O(1) bond lengths to 2.213 (7) Å. Correspondingly, the O(2)-C(1) bond (1.26 (1) Å) is longer than the O(1)-C(1) bond (1.24 (1) Å). A similar trend has been also observed in the structure of **1**. It seems that, as a monomethyl carbonate oxygen binds to Zn²⁺ more tightly, the O-C bond becomes longer.

Perchlorate oxygen (O(11)) is situated in the close proximity of the sixth coordination site of the terminal Zn(2) atom. The distance between Zn(2) and O(11) is found to be 3.29 (2) Å.

[Zn(O₂COCH₃)(Me₄[14]aneN₄)](ClO₄) (**3**). The molecular structure of **3** is quite different from those of **1** and **2** as is seen in Figure 3. It is a mononuclear complex involving unidentate CH₃OCO₂⁻, as expected from IR spectral data.¹ Coordination geometry about Zn is of the trigonal-bipyramidal type. The N(2) and N(4) atoms sit at the apical positions. Axial bonds are longer than in-plane bonds and have tilts from a normal to the trigonal plane owing to the rigidity of the macrocyclic ligand, the N(2)-Zn-N(4) angle being 166.2 (1)°. All four methyl groups are disposed toward the same side as the CH₃OCO₂⁻ ligand, and the macrocycle is folded by the steric repulsion between the macrocycle and the CH₃OCO₂⁻ ligand. The similar trigonal-bipyramidal coordination of the Me₄[14]aneN₄ ligand has been proposed as the solution structure of [ZnX(Me₄[14]aneN₄)]⁺ (X = Cl⁻, Br⁻, I⁻, NCS⁻, ClO₄⁻) on the basis of an NMR study, though the crystal structures containing this macrocycle are reported to have the square-pyramidal geometry.^{9,10} In compound **3**, the monomethyl carbonate ion does not act as a bridging ligand. It is because the methyl groups hinder sterically access of two Zn(Me₄[14]aneN₄) units close enough to make a bridge. The monomethyl carbonate in **3** is coordinated more tightly to Zn²⁺ than in **1** and **2**, as evidenced by the shorter Zn-O distance (1.965 (3) Å).

Variety of Zn-O Bond Lengths. From the viewpoint of coordination stereochemistry, it is interesting to note that the Zn-O bond distances found in this study span a wide range, from 1.965 (3) to 2.227 (3) Å, depending on the coordination geometries and the ligation modes of CH₃OCO₂⁻. They are classified into three groups. The shortest Zn-O distances, ca. 2.0 Å, were found in the five-coordinate structures (Zn(2)-O(2) in **2** = 2.034 (6), Zn-O(1) in **3** = 1.965 (3) Å). On the other hand, the longest distances, ca. 2.2 Å, were observed in the tetragonal six-coordinate complexes (Zn(2)-O(2) in **1** = 2.227 (3), Zn(1)-O(1) in **2** = 2.213 (7) Å). As described previously, the coordination geometry about Zn(1) in **1** is taken as intermediate between the above two structures. Concomitantly, its Zn-O bond takes an intermediate value (Zn(1)-O(1) in **1** = 2.143 (3) Å). The same trend can be seen in structures of aquazinc(II) complexes. Zn-OH₂ bond distances in five-coordinate complexes with square-pyramidal geometry, [Zn(acac)₂(OH₂)]¹¹ and [Zn(N,N'-bis(salicylidene)-ethylenediamine)(OH₂)]¹² are reported to be ca. 2.0 Å, whereas that in a tetragonal six-coordinate complex, [Zn(8-hydroxy-

(8) In the case of the *n*-BuOCO₂⁻ complex with [15]aneN₄, only a similar trimeric complex was obtained (see ref 1).

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quinoline)(OH₂)₂], lengthens to 2.263 (5) Å.¹³

The coordination mode of CH₃OCO₂⁻ also affects the Zn-O distance, and such a comparison is possible for the five-coordinate structures. The Zn-O length associated with unidentate CH₃O-CO₂⁻ (Zn-O(1) in **3** = 1.965 (3) Å) is slightly shorter than that involved in the bridge coordination (Zn(2)-O(2) in **2** = 2.034 (6) Å). The former value is close to Zn-O distance of 1.946 (6) Å found for a Zn(II) complex with unidentate CH₃CO₂⁻, [2-(2-benzothiazolyl)-6-[2-(2-thiophenyl)-2-azaethyl]pyridine](acetato)zinc(II).¹⁴

It has been suggested that there is a clear-cut difference in bond lengths between the tetrahedral and octahedral Zn-O bond.¹⁵ Yachandra et al. have also pointed out recently that there is a clear trend of increasing bond distance with increasing coordination number.¹⁶ The structural data for the present series of mono-methyl carbonato complexes show that the Zn-O bond lengthens in the following order, five-coordination with unidentate CH₃O-CO₂⁻ < five-coordination with bridging CH₃OCO₂⁻ < pseudo-six-coordination < tetragonally distorted octahedral six-coordination.

Chemical Consequences of Coordination of Tetraazacycloalkanes to Zn²⁺ on CO₂ Uptake. Two types of basic structure have been found in this study: (i) a linear chain structure with bridging monomethyl carbonate (**1** and **2**); (ii) a mononuclear structure with a unidentate monoalkyl carbonato ligand (**3**). The cavity

sizes of 14- and 15-membered macrocycles are appropriate to accommodate a Zn²⁺ ion in a planar fashion. To our knowledge, square-planar four-coordinate Zn(II) complexes are very rare and (phthalocyanato)- and (tetraphenylporphinato)zinc(II) are the only known examples.^{17,18} In general, a Zn²⁺ ion in square-planar array of four nitrogens tends to take up additional ligands at axial positions to form either five- or six-coordinate complex. Therefore, when Zn²⁺ is accommodated into the cavity of the [14]aneN₄ or [15]aneN₄ macrocycle in a planar fashion, its vacant axial sites provide a strong driving force for the coordination of monoalkyl carbonates. Such stereochemical consequences of coordination environments about Zn²⁺ are considered to be responsible for the efficient and facile uptake of CO₂.

In the case of the Me₄[14]aneN₄ system, CO₂ is fixed into the Zn(II) complex as unidentate monomethyl carbonate. Steric constraint provided by four methyl groups prevents bridge coordination of monomethyl carbonate. However, the Me₄[14]aneN₄ ligand folds easily and is impossible to deform tetrahedrally. As a consequence, the complex attains a near trigonal-bipyramidal geometry by taking up CH₃OCO₂⁻ at the fifth coordination site.

Acknowledgment. The present research was partly supported by Grant-in-Aid for Scientific Research No. 58470039 from the Ministry of Education, Science and Culture, Japan.

Registry No. 1, 94249-74-8; 2, 94249-70-4; 3, 94249-72-6.

Supplementary Material Available: Tables of hydrogen atomic coordinates, full bond lengths and angles, and structure factors and stereoscopic views of the crystal structures of complexes 1-3 (62 pages). Ordering information is given on any current masthead page.

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Structural Characterization and Infrared Studies of Tungsten Bromo Carbonyl Compounds

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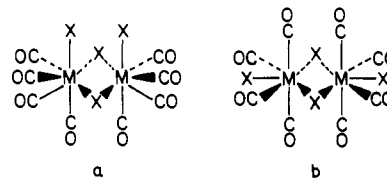
Received April 18, 1984

The syntheses of [WBr(CO)₄]₂(μ-Br)₂ (**1**) and (CO)₄W(μ-Br)₃WBr(CO)₃ (**2**) are described. Compound **1** crystallizes in the monoclinic space group C2/m with cell parameters *a* = 11.244 (9) Å, *b* = 8.172 (5) Å, *c* = 9.135 (7) Å, β = 94.58 (6)°, *V* = 837 (2) Å³, and *Z* = 2. The general structure of **1** may be described as that of two edge-sharing capped octahedra having an overall C_{2h} point symmetry but with virtual C_{3v} symmetry about each metal center. Compound **2** crystallizes in space group Pnma with lattice parameters *a* = 20.249 (4) Å, *b* = 8.058 (2) Å, *c* = 9.670 (2) Å, *V* = 1578 (1) Å³, and *Z* = 4. The complex has C_s symmetry, with three Br bridges between two W atoms, four CO groups on one end and three CO groups and a bromine atom on the other. In both compounds the metal atoms are seven-coordinate. In **1** the arrangement is that of a *fac*-WBr₃(CO)₃ octahedron capped by a CO on the (CO)₃ face, while in **2** there is a 4-3 arrangement, either (CO)₄WBr₃ or (CO)₃BrWBr₃, about each metal atom. The solution infrared spectra of these complexes are shown to be compatible with their solid-state structures.

Introduction

The halo carbonyls of the group 6¹² metals in their formal oxidation states of II, viz., [MX₂(CO)₄]_x compounds with M = Mo or W and X = Cl, Br, or I, are useful starting materials in many interesting reactions.¹⁻³ Much of the pioneering work on the preparation of these compounds as well as early studies of their reactivity is due to Colton and co-workers.⁴ If these compounds were to be formulated as mononuclear, they would be 16-electron species; dinuclear structures, with halogen bridges, such as a⁵ and

b¹ have therefore been suggested. However, there has still not



been any definitive structural proof for any of these compounds, nor can it be said that infrared evidence has been invoked cogently in favor of any particular structure. In view of the fact that compounds of this class have been used in this laboratory for synthetic purposes on several occasions,^{2,6} and because they are

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