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SYNTHESIS AND CRYSTAL STRUCTURES OF TWO DICHLORO-BRIDGED DIMERIC METAL COMPLEXES OF 1,4,7-TRIAZACYCLODECANE: $[Zn_2(tacd)_2Cl_2](ClO_4)_2$ AND $[Cu_2(tacd)_2Cl_2](ClO_4)_2$

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Abstract—Two dichloro-bridged dimeric metal complexes of 1,4,7-triazacyclodecane (tacd), $[Zn_2(tacd)_2Cl_2](ClO_4)_2$ (**1**) and $[Cu_2(tacd)_2Cl_2](ClO_4)_2$ (**2**), have been prepared and characterized by X-ray crystallography. Each zinc(II) atom in **1** is surrounded by a distorted trigonal-bipyramidal N_3Cl_2 environment with Zn—N and Zn—Cl bond lengths at ranges of 2.038(5) to 2.114(4) Å and 2.292(1) to 2.715(2) Å, respectively. Each copper(II) atom in **2** adopts a highly distorted trigonal-bipyramidal N_3Cl_2 coordination geometry with the Cu—N and Cu—Cl bond lengths at ranges of 2.011(4) to 2.180(4) Å and 2.323(3) to 2.353(1) Å, respectively.

Tridentate macrocyclic amines have attracted considerable interest in the synthesis of metal complexes of biological relevance. In the past two decades, a large number of metal complexes containing this kind of tripodal ligand have been prepared and extensively investigated in structures and properties, especially the two macrocyclic ligands of this type, the nine-membered triazacyclonane and twelve-membered triazacyclododecane, as well as their trimethylated derivatives are most frequently employed.[1-6] Recently, several monomeric metal complexes comprising the much less well-known ten-membered macrocycle triazacyclodecane (tacd) have been prepared and structurally characterized.[7-9] The nine- and twelve-membered macrocyclic triamine ligands can form either only five- or only six-membered chelate rings, respectively. In contrast, the ten-membered macrocyclic triamine ligand can form both five- and six-membered chelate rings with metal ions, hence it may exhibit different coordination geometry with more flexibility. Previously we have prepared and characterized two monomeric complexes, $[Zn(tacd)_2](ClO_4)_2$ and $[Cu(tacd)_2]Br_2 \cdot 4H_2O$.[9] In this paper, we report the preparation and structural characterization of two dichloro-bridged dimeric metal complexes of tacd, namely $[Zn_2(tacd)_2Cl_2](ClO_4)_2$ (**1**) and $[Cu_2(tacd)_2Cl_2](ClO_4)_2$ (**2**).

EXPERIMENTAL

The tacd·3HCl was synthesized by a modification of the literature method.[10,11] The C, H and N microanalyses were carried out on a Perkin–Elmer 250Q elemental analyzer. FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Nicolet 5DX spectrometer.

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Preparation

To an aqueous ethanolic solution (12 cm^{-3}, 90%) containing tacd·3HCl (0.248 g, 1.0 mmol) was added Zn(ClO$_4$)$_2$·6H$_2$O (0.185 g, 1.0 mmol) with stirring, and the mixture was adjusted to pH ~ 5.5 with slow addition of 1 N NaOH solution. A small quantity of precipitate was filtered and the resulting colourless solution was then allowed to stand in air at room temperature for several days, giving colourless polyhedral crystals of complex **1**. Found: C, 24.4; H, 5.0; N, 12.3. Calc. for $C_{14}H_{34}Cl_4Zn_2N_6O_8$: C, 24.5; H, 5.0; N, 12.2%. IR data (cm^{-1}): 3282s, 3247s, 3226s, 3121s, 2917s, 2868s, 2811w, 1482m, 1477s, 1370w, 1309w, 1278w, 1145vs, 1110vs, 1082vs, 1004m, 976s, 878w, 821s, 632s.

To an aqueous ethanolic solution (10 cm^{-3}, 90%) containing tacd·3HCl (0.248 g, 1.0 mmol) was added Cu(CH$_3$CO$_2$)$_2$·H$_2$O (0.200 g, 1.0 mmol), and followed with NaClO$_4$ (0.07 g, 0.5 mmol). The resulting green solution was stirred for 20 min at 50°C and then allowed to stand in air at room temperature. After several days, dark green prismatic crystals of complex **2** were obtained. Found: C, 24.5; H, 5.0; N, 12.1. Calc. for $C_{14}H_{34}Cl_4Cu_2N_6O_8$ (**2**): C, 24.6; H, 5.0; N, 12.3%. IR data (cm^{-1}): 3247vs, 2959m, 2917m, 2860m, 1632w, 1482w, 1447m, 1363w, 1342w, 1307w, 1264w, 1145vs, 1117vs, 1098vs, 1025m, 990s, 969m, 885m, 842m, 800m, 632s.

Crystallography

Diffraction intensities for complexes **1** and **2** were collected at room temperature (21°C) on the Rigaku AFC5R and a Siemens R3m/V diffractometer, respectively. Lp and absorption corrections were applied. The structures were solved with direct methods using SAPI-91[12] and refined with full-matrix least-squares technique using SHELXTL-PC program package[13] (detailed parameters given in Table 1). The non-hydrogen atoms were refined anisotropically, except the oxygen atoms of the two-fold orientationally disordered perchlorate anions

Table 1. Crystallographic data for complex **1** and **2**

Complex	**1**	**2**
Mol. formula	$C_{14}H_{34}Cl_4Zn_2N_6O_8$	$C_{14}H_{34}Cl_4Cu_2N_6O_8$
Mol. wt.	687.03	683.36
Colour and habit	colourless polyhedral	dark green prismatic
System	monoclinic	monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
Cell parameters		
a (Å)	8.046(2)	8.602(2)
b (Å)	11.479(2)	13.078(3)
c (Å)	14.291(3)	11.237(3)
β (°)	99.26(3)	95.15(2)
V (A^3)	1302.7	1259.0
Z	2	2
F(000)	704	700
Density (g cm^{-3})	1.751	1.800
Temperature (°C)	21°C	21°C
Diffractometer	Rigaku AFC5R	Siemens R3m/V
Radiation	Mo-K_α (λ = 0.71073 Å)	Mo-K_α (λ = 0.71073 Å)
Intensity variation (%)	1.50	1.25
Absorption coef. (cm^{-1})	23.03	21.65
Crystal size (mm^3)	0.36 × 0.38 × 0.44	0.33 × 0.36 × 0.42
Collection range (°)	$3 \leqslant 2\theta \leqslant 55$	$5 \leqslant 2\theta \leqslant 55$
R_{int}	0.010	0.012
Data collected	2775	3093
Unique data	2587	2907
Obs. data	2387 ($I \geqslant 3\sigma(I)$)	2083 ($I \geqslant 2\sigma(I)$)
Parameters refined	180	154
R (R_w) value	0.0641 (0.0745)	0.0455 (0.0516)
Goodness-of-fit	2.65	1.24
Weighting scheme	$w^{-1} = \sigma^2(F)+0.0002F^2$	$w^{-1} = \sigma^2(F)+0.0001F^2$

in complex **1** which were subjected to inter-atomic distance constraints of Cl—O = 1.41 ± 0.01 Å and O···O = 2.35 ± 0.01 Å, assigned site occupancy factors of 0.5, and refined isotropically. The alkyl hydrogen atoms were generated geometrically (C—H = 0.96 Å) and the amine hydrogen atoms were located from difference maps, assigned the same isotropic temperature factors of $U = 0.08$ Å^2, and included in the structure-factor calculations. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[14] The final dis-

Table 2. Selected bonded lengths (Å) and bond angles (°)

Complex **1**			
Zn(1)—Cl(1)	2.292(1)	Zn(1)—N(1)	2.114(5)
Zn(1)—N(2)	2.038(5)	Zn(1)—N(3)	2.039(5)
Zn(1)—Cl(1a)	2.715(2)	N(1)—C(1)	1.495(10)
N(1)—C(7)	1.507(9)	N(2)—C(2)	1.476(8)
N(2)—C(3)	1.487(8)	N(3)—C(5)	1.488(9)
N(3)—C(6)	1.477(8)	C(1)—C(1)	1.471(14)
C(3)—C(4)	1.507(9)	C(4)—C(5)	1.520(10)
C(6)—C(7)	1.503(12)		
Cl(1)—Zn(1)—N(1)	98.0(1)	Cl(1)—Zn(1)—N(2)	135.0(1)
N(1)—Zn(1)—N(2)	84.2(2)	Cl(1)—Zn(1)—N(3)	123.0(1)
N(1)—Zn(1)—N(3)	85.2(2)	N(2)—Zn(1)—N(3)	102.0(2)
Cl(1)—Zn(1)—Cl(1a)	88.5(1)	N(1)—Zn(1)—Cl(1a)	173.3(1)
N(2)—Zn(1)—Cl(1a)	90.2(1)	N(3)—Zn(1)—Cl(1a)	92.4(1)
Zn(1)—Cl(1)—Zn(1a)	91.5(1)	Zn(1)—N(1)—C(1)	103.2(5)
Zn(1)—N(1)—C(7)	107.3(4)	Zn(1)—N(2)—C(2)	110.0(4)
Zn(1)—N(2)—C(3)	111.9(4)	Zn(1)—N(3)—C(5)	113.0(4)
Zn(1)—N(3)—C(6)	108.3(4)	C(1)—N(1)—C(7)	113.5(6)
CC(2)—N(2)—C(3)	113.7(5)	C(5)—N(3)—C(6)	114.0(5)
N(1)—C(1)—C(2)	111.6(7)	N(2)—C(2)—C(1)	114.1(6)
N(2)—C(3)—C(4)	115.0(5)	C(3)—C(4)—C(5)	118.4(5)
N(3)—C(5)—C(4)	115.9(5)	N(3)—C(6)—C(7)	113.2(5)
N(1)—C(7)—C(6)	109.7(6)		
Complex **2**			
Cu(1)—Cl(1)	2.353(1)	Cu(1)—N(1)	2.011(4)
Cu(1)—N(2)	2.180(4)	Cu(1)—N(3)	2.012(4)
Cu(1)—Cl(1a)	2.323(1)	N(1)—C(1)	1.500(8)
N(1)—C(7)	1.466(7)	N(2)—C(2)	1.468(7)
N(2)—C(3)	1.475(7)	N(3)—C(5)	1.490(6)
N(3)—C(6)	1.482(6)	C(1)—C(2)	1.456(10)
C(3)—C(4)	1.526(8)	C(4)—C(5)	1.518(7)
C(6)—C(7)	1.517(8)		
Cl(1)—Cu(1)—N(1)	92.0(1)	Cl(1)—Cu(1)—N(2)	102.8(1)
N(1)—Cu(1)—N(2)	83.0(2)	Cl(1)—Cu(1)—N(3)	158.0(1)
N(1)—Cu(1)—N(3)	85.7(1)	N(2)—Cu(1)—N(3)	98.6(1)
Cl(1)—Cu(1)—Cl(1a)	87.8(1)	N(1)—Cu(1)—Cl(1a)	176.3(1)
N(2)—Cu(1)—Cl(1a)	100.6(1)	N(3)—Cu(1)—Cl(1a)	93.1(1)
Cu(1)—Cl(1)—Cu(1a)	92.2(1)	Cu(1)—N(1)—C(1)	105.3(3)
Cu(1)—N(1)—C(7)	111.2(3)	Cu(1)—N(3)—C(5)	113.7(3)
Cu(1)—N(2)—C(2)	107.1(3)	Cu(1)—N(2)—C(3)	113.2(3)
Cu(1)—N(3)—C(6)	108.5(3)	C(1)—N(1)—C(7)	112.2(4)
C(2)—N(2)—C(3)	114.6(4)	C(5)—N(3)—C(6)	114.9(4)
N(1)—C(1)—C(2)	112.8(5)	N(2)—C(2)—C(1)	113.2(5)
N(2)—C(3)—C(4)	115.0(4)	C(3)—C(4)—C(5)	116.1(4)
N(3)—C(5)—C(4)	116.2(4)	N(3)—C(6)—C(7)	112.0(4)
N(1)—C(7)—C(6)	109.9(5)		

Symmetry code for **1**: (a) $-x$, $-y$, $-z$; for **2**: (a) $-x$, $-y$, $-z$.

crepancy indices and other parameters at the conclusion of refinement are summarized in Table 1, and selected inter-atomic distances and bond angles in Table 2.

Supplementary material including non-hydrogen and hydrogen atomic coordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre, and observed and calculated structure factors are available upon request from the corresponding author.

RESULTS AND DISCUSSION

The crystal structure of complex **1** consists of discrete $[Zn_2(tacd)_2Cl_2]^{2+}$ cations and perchlorate anions. As illustrated in Fig. 1, the two centrosymmetrically related zinc atoms being separated by a non-bonded distance of 3.597(1) Å, are bridged by a pair of chlorides and terminated by two tacd ligands. Each zinc atom is coordinated by a tacd ligand and two chlorides in a distorted trigonal-bipyramidal N_3Cl_2 environment with one chlorine and one nitrogen atom occupying the axial positions [Zn(1)—Cl(1a) = 2.715(2) Å, Zn(1)—N(1) = 2.114(5) Å]. The Zn—N bond lengths at the equatorial positions are *ca* 2.038(5) Å, slightly shorter than that of the axial Zn(1)—N(1) bond. The chloro-bridges are unsymmetrical with the Zn—Cl bonds at 2.292(1) and 2.715(1) Å, in which the longer Zn—Cl bond occupies the axial position in the coordination polyhedron. The Zn—Cl—Zn bond angle is at 91.5(1)°. Similar dichloro-bridges have been found in some copper(II) complexes.[15–17] In contrast, no dichloro-bridged dimeric zinc complexes with the metal atoms in pentacoordination have been reported so far.[18] Hence complex **1** presents a new structural variety among dizinc chemistry. It is worthy of note that in complex **1** the N—Zn—N bond angles in the six- and five-membered chelate rings have the values of 102.0(2) and 84.7 ± 0.5°, respectively, which are both significantly larger than the corresponding values [85.9(1) and 81.6 ± 0.4°, respectively] found for the monomeric zinc complex $[Zn(tacd)_2](ClO_4)_2$.[9] These facts demonstrate clearly that the structure of the ten-membered macrocyclic ligand tacd is very flexible in coordination to metal ions.

The crystal structure of complex **2** comprises discrete $[Cu_2(tacd)_2Cl_2]^{2+}$ cations and perchlorate anions. As illustrated in Fig. 2, a pair of copper(II) atoms, being separated at a non-bonded distance of 3.369(1) Å, are bridged by two chlorides into a dimeric structure, which also possesses a crystallographic inversion center. In the dimeric structure the chloro-bridges are virtually symmetrical with the Cu—Cl bond lengths at 2.323(4) and 2.353(5) Å, and the Cu—Cl—Cu bond angle at 92.2(1)°. In contrast, in pentacoordinate dichloro-bridged copper(II) complexes the Cu—Cl—Cu bridges are commonly unsymmetrical with one Cu—Cl bond significantly longer than the other.[15–17] Each copper(II) atom in complex **2** is coordinated in a distorted trigonal-bipyramidal N_3Cl_2 environment with one chlorine and one nitrogen atom at the apical positions [Cu(1)—Cl(1a) = 2.323(1) Å and Cu(1)—N(1) = 2.011(4) Å, Cl(1a)—Cu(1)—N(1) = 176.3(1)°]. The equatorial Cu—N bond lengths are in a range of 2.012(4) to 2.180(4) Å. The distortion of the trigonal-bipyramidal polyhedron is highly towards square-pyramidal, as evidenced by the usually large equatorial Cl(1)—Cu(1)—N(3) bond angle [158.0(1)°], which is much larger than the corresponding value [Cl(1)—Zn(1)—N(2) = 135.0(1)°] found for complex **1**. Presumably the greater distortion may be caused by the open shell d^9 electron configuration of the copper(II) ions in complex **2** in comparison with the closed shell d^{10} configuration of the zinc ions in complex **1**. Similar

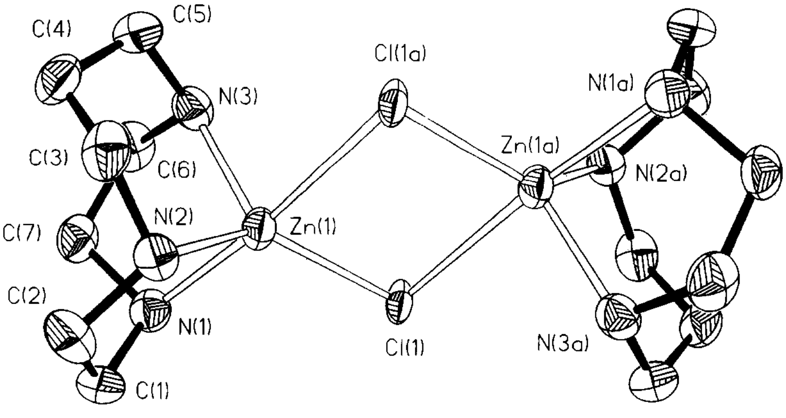

Fig. 1. ORTEP drawing (35% probability) of the dimeric $[Zn_2(tacd)_2Cl_2]^{2+}$ cation in **1** and atom-numbering scheme. Symmetry code: (a) $-x$, $-y$, $-z$.

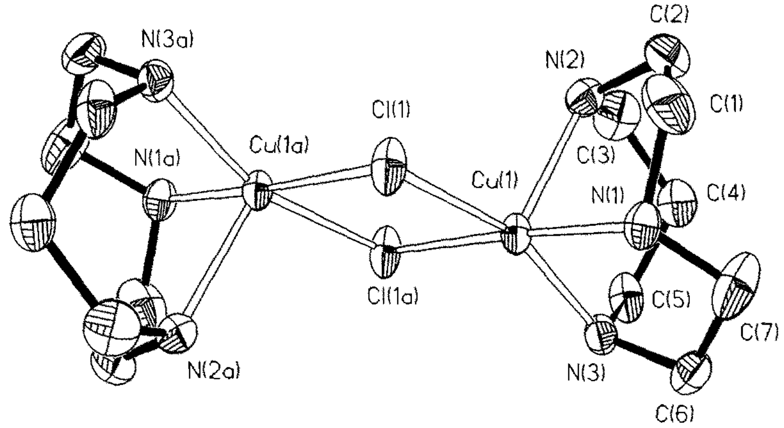

Fig. 2. ORTEP drawing (35% probability) of the dimeric $[Cu_2(tacd)_2Cl_2]^{2+}$ cation in **2** and atom-numbering scheme. Symmetry code: (a) $-x$, $-y$, $-z$.

to the case of complex **1**, the N(2)—Cu(1)—N(3) bond angle in the six-membered chelate ring is significantly larger than those of the five-membered chelate rings [98.6(1) *vs* 85.7(1) or 83.0(1)°]. The five- and six-membered chelate rings of tacd in complex **2** exhibit skew and chair conformations, respectively, analogous to those found for complex **1** and the monomeric metal complexes of tacd.[7–9]

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