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PREPARATION AND X-RAY STRUCTURE OF A NEW $[\mu_2\text{-OXO}]$ BRIDGED MACROCYCLIC DICADMIUM(II) COMPLEX

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PREPARATION AND X-RAY STRUCTURE OF A NEW μ_2 -OXO BRIDGED MACROCYCLIC DICADMIUM(II) COMPLEX

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A new macrocyclic binuclear cadmium(II) complex with pendant arms has been synthesized by the [2+2] Schiff base condensation of *tris*(3-aminopropyl)amine (trpn) with sodium 2,6-diformyl-4-bromophenolate (sdbp) in the presence of Cd^{2+} ion. The crystal structure of the complex $[\text{Cd}_2\text{L}](\text{ClO}_4)_2$ has been determined by X-ray methods. The complex crystallizes in the monoclinic system, space group $P2_1/c$ with $a = 11.922(3)$, $b = 16.207(3)$, $c = 23.229(3)$ Å, $\beta = 90.94(2)^\circ$, $V = 4488(2)$ Å³, $F(000) = 2352$, $Z = 4$, $D_c = 1.75$ g cm⁻³, $\mu = 28.86$ cm⁻¹, $R = 0.069$, $R_w = 0.071$. Each Cadmium lies at the centre of a very distorted octahedron composed of two oxygens of bridging phenoxy groups and four nitrogens from trpn. Coordination of phenoxy oxygens enhances the stability of the complex.

Keywords: cadmium; binuclear complex; polyazamacrocyclic; X-ray structure

INTRODUCTION

Although many studies have been reported on cadmium(II) macrocyclic complexes,^{1–3} only a few crystal structures of them are known, and most were found to be mononuclear complexes.^{4–8} We have reported the crystal structure of a binuclear cadmium(II) complex of a 24-membered macrocyclic complex, recently.⁹ In this paper we report the synthesis, characterization and X-ray structure of a new μ -oxo bridged binuclear cadmium(II) complex of a 28-membered macrocyclic complex with pendant arms (Figure 1) which was synthesized by

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a [2+2] Schiff base condensation of *tris*(3-aminopropyl)amine (trpn) with sodium 2,6-diformyl-4-bromophenolate (sdbp) in the presence of Cd^{2+} . To our knowledge, only few of these kinds of structures have hitherto been reported.

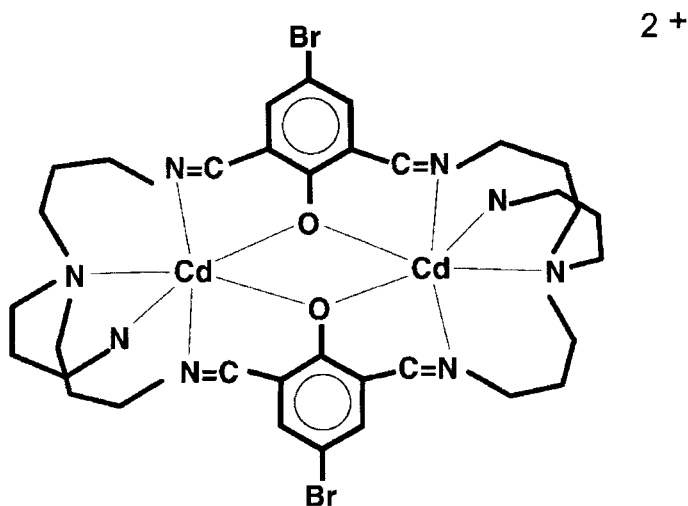


FIGURE 1 The binuclear complex cation $[\text{Cd}_2\text{L}]^{2+}$.

EXPERIMENTAL

All starting materials were of analytical purity. *Tris*(3-aminopropyl)amine (trpn) was prepared by a modified literature method.¹⁰ 2,6-Diformyl-4-bromophenol (dbp) was prepared using the method described in the literature.¹¹ Sodium 2,6-diformyl-4-bromophenolate (sdbp) was prepared by mixing equimolar amounts of dmp and NaOH in absolute ethanol. Solution electrical conductivity was measured with a BSD-A conductometer (Jiangsu, China) with a solution concentration of $\sim 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ in acetonitrile. IR spectra were measured in KBr discs using a Nicolet 5DX FT-IR spectrophotometer. Electronic spectra were recorded on a Shimadzu UV-240 spectrophotometer.

Preparation of $[\text{Cd}_2\text{L}](\text{ClO}_4)_2 \cdot 3\text{CH}_3\text{OH}$

To a stirred solution of sodium 2,6-diformyl-4-bromophenolate (0.1255 g, 0.5 mmol) and $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.2621 g, 0.625 mmol) in 20 cm^3 of absolute methanol was added dropwise a solution of *tris*(3-aminopropyl)amine (0.094 g, 0.5 mmol) in 10 cm^3 of absolute methanol at 0°C . After stirring the solution for

2 h at 35°C, the yellowish microcrystals of $[\text{Cd}_2\text{L}](\text{ClO}_4)_2 \cdot 3\text{CH}_3\text{OH}$ which had precipitated were filtered off, washed with methanol and dried *in vacuo*, with a yield of 75%. *Anal.* Calcd. for $\text{C}_{37}\text{H}_{60}\text{N}_8\text{O}_{13}\text{Cl}_2\text{Br}_2\text{Cd}_2$ (%): C, 34.94; H, 4.76; N, 8.81; Cd, 17.55. Found: C, 34.59; H, 4.55; N, 9.02; Cd, 17.30. IR (cm^{-1}): 3453 (br $\nu_{(\text{OH})}(\text{CH}_3\text{OH})$); 3294, 3354 (s, $\nu_{(\text{NH}_2)}$); 1641 (s, $\nu_{(\text{C}=\text{N})}$); 1540 (s, $\nu_{(\text{ph-O})}$); 1097 (s, $\nu_{(\text{ClO}_4)}$). UV-Vis (λ_{max} (nm), CH_3CN): 396 ($16333 \text{ M}^{-1} \text{ cm}^{-1}$); 248 (37866); 226 (49933). Λ_{M} (CH_3CN , 289 K): $262 \text{ S cm}^2 \text{ mol}^{-1}$. Yellowish crystals of $[\text{Cd}_2\text{L}](\text{ClO}_4)_2$ suitable for the X-ray structure determination were obtained by slow evaporation of the above filtrate at room temperature. **Caution.** Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with caution. The complexes described in this report have, so far, been found to be safe when used in small quantities.

Crystallographic data collection and solution of structure

Crystallographic data for the complex $[\text{Cd}_2\text{L}](\text{ClO}_4)_2$ are summarized in Table I. Diffraction data were collected on an on a Enraf-Nonius CAD4 diffractometer with graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) over the range $2 < 2\theta < 50^\circ$, with a ω - 2θ scan mode and with a ω scan width of $1.30 + 0.350 \tan\theta$, scan rate $5.49^\circ \text{ min}^{-1}$. The structure was solved by MITHRIL direct methods using the programs contained in the TEXSAN package. The remaining non-hydrogen atoms were located from a difference Fourier map. Hydrogen atoms were introduced in calculated positions but were not refined. All calculations were performed using the programs contained in the TEXSAN package.

TABLE I Crystal data and collection parameters for the complex

Formula	$\text{C}_{34}\text{H}_{48}\text{N}_8\text{O}_{10}\text{Cl}_2\text{Br}_2\text{Cd}_2$
Molecular weight	1184.33
Colour	yellowish
Crystal system	monoclinic
Space group	$P2_1/c$
$a(\text{\AA})$	11.922(3)
$b(\text{\AA})$	16.207(3)
$c(\text{\AA})$	23.229(3)
$\beta(\text{deg})$	90.94(2)
$V(\text{\AA}^3)$	4488(2)
Z	4
$D_c(\text{g cm}^{-3})$	1.75
$F(000)$	2352
$\mu(\text{cm}^{-1})$	28.86
Crystal dimensions (mm)	$0.20 \times 0.25 \times 0.30$
Radiation (\AA)	$\text{MoK}\alpha$ (0.71073)
Scan mode	ω - 2θ

TABLE I (Continued)

2 θ range (deg)	2 to 50.0
No. reflections measured	8587
No. reflections used ($I > 3\sigma(I)$)	1819
Variables	275
Final R , R_w	0.069, 0.071

RESULTS AND DISCUSSION

Spectroscopic characterization of the binuclear complex

In the infrared spectrum a strong peak at 1641 cm^{-1} corresponds to the C=N stretch. Symmetric and asymmetric stretching frequencies (3294 and 3354 cm^{-1}) for NH_2 groups are also present, but no strong peaks at $1650\text{--}1700\text{ cm}^{-1}$ for the carbonyl groups are found because two NH_2 and carbonyl groups have condensed into C=N bonds, whilst another NH_2 group is unchanged. A broad band at 3454 cm^{-1} characteristic of the OH group of CH_3OH showed that CH_3OH molecules exist in the crystalline complex, in agreement with elemental analysis. These CH_3OH molecules are lost during growth of single crystals of $[\text{Cd}_2\text{L}](\text{ClO}_4)_2$ for the X-ray structure determination. The strong peak at 1097 cm^{-1} indicates that ClO_4^- does not take part in coordination with Cd. This is also confirmed by the molar conductivity of the complex which is characteristic of a 2:1 electrolyte,¹² this indicates that the phenoxy oxygens are also coordinated to cadmium atoms. The three strong peaks in the UV region of the electronic spectrum are assigned to $\pi\text{--}\pi^*$ transitions of benzene rings and C=N groups.¹³

Description of the structure of $[\text{Cd}_2\text{L}](\text{ClO}_4)_2$

A perspective view of the $[\text{Cd}_2\text{L}]^{2+}$ cation is shown in Figure 2. Positional parameters, selected bond distances and angles are given in Tables II and Table III, respectively.

In Figure 2 it is seen that each Cd(II) atom is enclosed within the polyaza macrocycle. Each is coordinated by one amino nitrogen atom of the pendant arms, two imino nitrogen atoms, one nitrogen atom of the tertiary amine and two oxygen atoms of phenoxy groups to form a distorted octahedron. Around Cd(1), the amino nitrogen atom N(7) and imino nitrogen atoms N(2) and N(6) occupy equatorial positions and one phenoxy oxygen, O(2), deviates from the equatorial plane; the tertiary nitrogen N(1) and another phenoxy oxygen, O(1), occupy approximately axial positions. Around Cd(2), the amino nitrogen atom

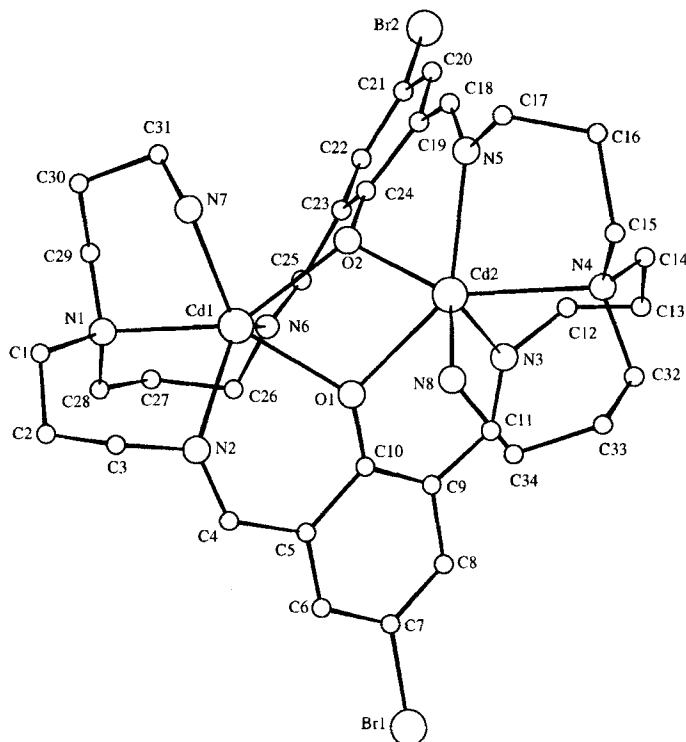


FIGURE 2 Perspective view of the complex showing the atom labelling scheme.

TABLE II Positional parameters for the complex

Atom	x/a	y/b	z/c	$B(\text{\AA}^2)$
Cd(1)	0.3604(2)	0.1792(2)	0.1249(1)	4.9(10)
Cd(2)	0.1364(2)	0.2487(2)	0.0233(1)	4.6(1)
Br(1)	-0.1548(3)	0.0805(3)	0.2916(2)	9.5(3)
Br(2)	0.4261(3)	0.6505(2)	0.0761(2)	6.1(2)
O(1)	0.172(1)	0.175(1)	0.1097(8)	5.5(5)
O(2)	0.304(1)	0.290(1)	0.0658(8)	5.0(5)
N(1)	0.520(2)	0.146(2)	0.190(1)	5.7(6)
N(2)	0.299(2)	0.049(2)	0.154(1)	5.7(6)
N(3)	0.032(2)	0.318(2)	0.090(1)	5.2(6)
N(4)	-0.026(2)	0.287(2)	-0.041(1)	5.7(6)
N(5)	0.228(2)	0.324(2)	-0.047(1)	4.7(5)
N(6)	0.344(2)	0.287(2)	0.186(1)	5.9(6)
N(7)	0.493(2)	0.178(2)	0.056(1)	6.2(6)
N(8)	0.062(3)	0.124(2)	0.003(1)	11(1)
C(1)	0.559(3)	0.061(2)	0.179(2)	7(1)
C(2)	0.482(2)	-0.008(2)	0.189(1)	7.3(9)
C(3)	0.385(3)	-0.017(2)	0.146(2)	9(1)
C(4)	0.209(3)	0.029(2)	0.178(1)	6.7(9)
C(5)	0.116(2)	0.085(2)	0.185(1)	5.2(7)

TABLE II (Continued)

Atom	xa	y/b	z/c	$BB(\text{\AA}^2)$
C(6)	0.040(3)	0.063(2)	0.224(1)	6.7(9)
C(7)	-0.050(2)	0.115(2)	0.237(1)	5.8(8)
C(8)	-0.062(2)	0.187(2)	0.207(1)	5.5(7)
C(9)	0.015(2)	0.211(2)	0.164(1)	5.0(7)
C(10)	0.103(2)	0.160(2)	0.149(1)	5.6(8)
C(11)	-0.009(2)	0.289(2)	0.139(1)	4.5(7)
C(12)	0.001(2)	0.405(2)	0.070(1)	6.3(8)
C(13)	-0.086(2)	0.405(2)	0.027(2)	6.4(8)
C(14)	-0.051(2)	0.374(2)	-0.032(1)	5.8(8)
C(15)	-0.003(2)	0.268(2)	-0.100(2)	7.2(9)
C(16)	0.090(2)	0.321(2)	-0.129(1)	6.5(8)
C(17)	0.206(2)	0.300(2)	-0.106(1)	6.0(8)
C(18)	0.290(2)	0.387(2)	-0.035(1)	4.5(7)
C(19)	0.321(2)	0.422(2)	0.018(1)	4.5(7)
C(20)	0.354(2)	0.502(2)	0.019(1)	4.2(6)
C(21)	0.384(2)	0.538(2)	0.072(1)	4.3(6)
C(22)	0.381(2)	0.490(2)	0.123(1)	4.1(7)
C(23)	0.353(2)	0.405(2)	0.121(1)	2.7(5)
C(24)	0.328(2)	0.368(2)	0.068(1)	3.6(6)
C(25)	0.346(2)	0.364(2)	0.179(1)	5.7(8)
C(26)	0.339(2)	0.267(2)	0.250(1)	6.3(8)
C(27)	0.449(3)	0.234(2)	0.271(1)	8(1)
C(28)	0.490(3)	0.153(2)	0.250(2)	8(1)
C(29)	0.608(3)	0.212(2)	0.179(2)	8(1)
C(30)	0.661(2)	0.205(2)	0.120(1)	6.4(8)
C(31)	0.582(2)	0.233(2)	0.069(1)	6.3(8)
C(32)	-0.131(2)	0.238(2)	-0.021(1)	6.7(8)
C(33)	-0.132(3)	0.147(3)	-0.030(2)	10(1)
C(34)	-0.059(3)	0.108(3)	0.014(2)	10(1)

TABLE III Selected bond distances (\AA) and angles ($^\circ$) for the complex

Cd(1)—N(6)	2.27(3)	Cd(2)—N(8)	2.25(3)
Cd(1)—N(7)	2.28(2)	Cd(2)—N(3)	2.30(2)
Cd(1)—N(2)	2.34(3)	Cd(2)—N(5)	2.33(2)
Cd(1)—N(1)	2.47(2)	Cd(2)—N(4)	2.50(2)
Cd(1)—O(1)	2.27(2)	Cd(2)—O(1)	2.37(2)
Cd(1)—O(2)	2.36(2)	Cd(2)—O(2)	2.31(2)
O(1)—Cd(1)—N(7)	126.1(8)	N(3)—Cd(2)—N(5)	118.9(8)
O(1)—Cd(1)—N(2)	72.8(8)	N(3)—Cd(2)—O(1)	76.3(8)
O(1)—Cd(1)—O(2)	70.1(6)	N(3)—Cd(2)—N(4)	82.1(8)
O(1)—Cd(1)—N(1)	147.1(7)	N(5)—Cd(2)—O(2)	74.6(7)
N(7)—Cd(1)—N(2)	114.6(9)	O(2)—Cd(2)—O(1)	69.2(6)
N(7)—Cd(1)—O(2)	78.0(7)	O(2)—Cd(2)—N(4)	146.9(7)
N(7)—Cd(1)—N(1)	83.7(8)	N(5)—Cd(2)—O(1)	141.3(7)
N(2)—Cd(1)—O(2)	140.3(7)	N(5)—Cd(2)—N(4)	79.8(8)
N(2)—Cd(1)—N(1)	82.7(8)	O(1)—Cd(2)—N(4)	138.9(7)
O(2)—Cd(1)—N(1)	137.0(7)	N(8)—Cd(2)—N(3)	112(1)
N(6)—Cd(1)—O(1)	91.4(7)	N(8)—Cd(2)—O(2)	133(1)
N(6)—Cd(1)—N(7)	121.3(9)	N(8)—Cd(2)—N(5)	121(1)
N(6)—Cd(1)—N(2)	119(1)	N(8)—Cd(2)—O(1)	78(1)
N(6)—Cd(1)—O(2)	75.5(8)	N(8)—Cd(2)—N(4)	78(1)
N(6)—Cd(1)—N(1)	81.7(8)	N(3)—Cd(2)—O(2)	92.2(7)

N(8) and imino nitrogen atoms N(3) and N(5) occupy equatorial positions and one phenoxy oxygen, O(1), deviates from the equatorial plane, the tertiary nitrogen N(4) and another phenoxy oxygen, O(2), occupy approximately axial positions. Cd—O(1) and Cd—O(2) are between 2.27 and 2.37 Å, being normal coordination bonds. The distances between Cd and amino nitrogen atoms are in the range 2.25~2.28 Å, which is shorter than standard Cd—N bond distance of 2.33 ± 0.005 Å.¹⁴ This means that the amino groups are strongly coordinated to Cd(II). Cd—N(imino) bonds are in the range 2.30~2.34 Å, being normal coordination bonds. Conversely, the two bond distances between cadmium and the tertiary nitrogens are ca 2.50 Å, implying a weak interaction between Cd(II) and the bridgehead nitrogen atoms. The long Cd(1)...Cd(2) distance (3.711 Å) indicates that there is no interaction between the two metal atoms. All the angles —N(6)Cd(1)N(2) , —N(6)Cd(1)N(7) , —N(7)Cd(1)N(2) are ca 120°. Cd(II) lies in the centre of the plane composed of N(2), N(6), N(7) but beneath it by 0.29 Å; N(1) lies 2.18 Å above the plane and O(1) and O(2) beneath it by 2.22 and 2.01 Å respectively. A analogous complex, $[\text{Cu}_2\text{L}'(\text{OH})](\text{ClO}_4)_3$,¹⁵ synthesized by a [2+2] Schiff base condensation of tris(2-aminoethyl)amine with isophthalic aldehyde in the presence of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ is unstable. However, the flexibility of the carbon chain strengthens the coordination ability of bridgehead nitrogen atoms and the phenoxy oxygen atoms bridging the two Cd(II) enhances the stability of the complex reported here.

Acknowledgments

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