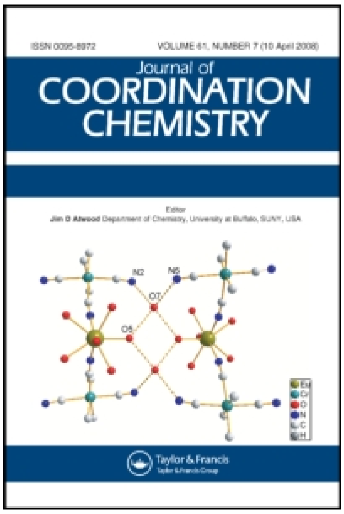

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Synthesis and x-ray crystal structure of a 24-membered macrocyclic binuclear cadmium(ii) complex with pendant arms

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SYNTHESIS AND X-RAY CRYSTAL STRUCTURE OF A 24-MEMBERED MACROCYCLIC BINUCLEAR CADMIUM(II) COMPLEX WITH PENDANT ARMS

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A new binuclear cadmium(II) macrocyclic complex has been synthesized by [2 + 2] Schiff base condensation of *tris*(2-aminoethyl)amine (tren) with sodium 2,6-diformyl-4-bromophenolate (sdbp) in the presence of Cd^{2+} ion. The crystal structure of the complex $[Cd_2L](ClO_4)_2{\cdot}0.5CH_3OH$ has been determined by X-ray methods. Crystals are monoclinic, space group $P2_1/c$ with a = 11.633(15), b = 16.370(2), c = 21.193(2) Å, β = 96.121(12)°, $Z = 4$, $V = 4013.0(8)$ Å^3, $F(000) = 2180$, $D_c = 1.841$ g cm^{-3}, $\mu = 32.46$ cm^{-1}, R = 0.049, R_w = 0.069. Two cadmium(II) ions are bridged by two μ_2-phenoxy oxygen atoms. Each cadmium lies in a N_4O_2 coordination environment. Coordination geometry around Cd(II) is a capped trigonal bipyramid. Coordination of phenoxy oxygens and terminal amino groups enhances the stability of the complex.

Keywords: cadmium; binuclear complex; polyazamacrocycle; 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 28-membered macrocyclic complex. [9]

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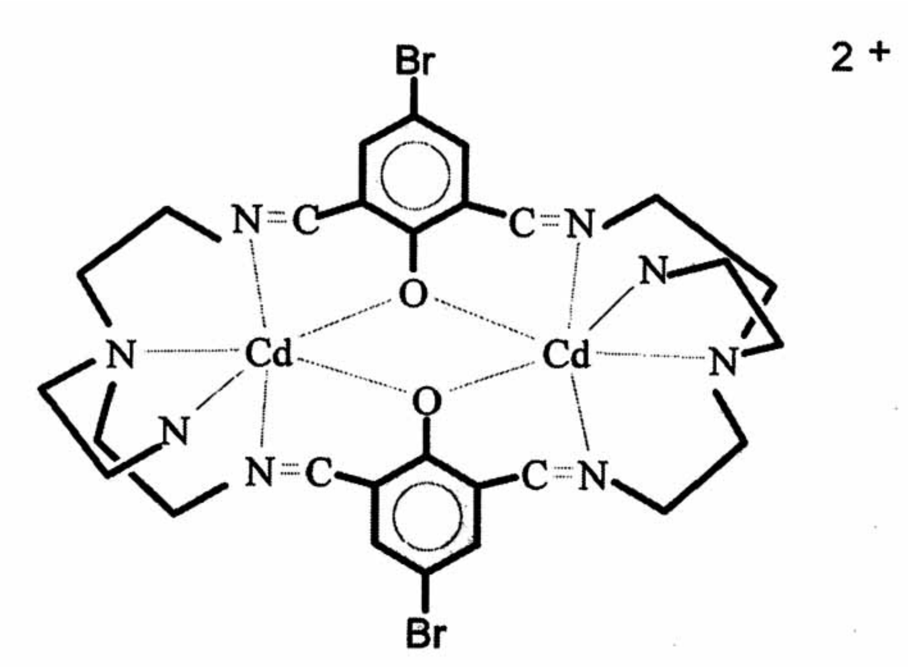
In this paper we report the synthesis, characterization and X-ray structure of a new μ-oxo bridged binuclear cadmium(II) complex of a 24-membered macrocyclic complex with pendant arms, **1**, which was synthesized by [2 + 2] Schiff base condensation of *tris*(2-aminoethyl)amine (tren) with sodium 2,6-diformyl-4-bromophenolate (sdbp) in the presence of Cd^{2+}. To our knowledge, few of these kinds of structures have been reported.

EXPERIMENTAL

All starting materials were of analytical purity. *Tris*(2-aminoethyl)amine (tren) was obtained from Aldrich and used without further purification. 2,6-Diformyl-4-bromophenol (dbp) was prepared using a method described in the literature. [10] 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 $\sim 1.0 \times 10^{-3}$ 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.



$[Cd_2L](ClO_4)_2{\cdot}2CH_3OH$.

To a stirred solution of sodium 2,6-diformyl-4-bromophenolate (0.1255 g, 0.5 mmol) and $Cd(ClO_4)_2{\cdot}6H_2O$ (0.2621 g, 0.625 mmol) in 20 cm^3 of absolute methanol was added dropwise a solution of *tris*(2-aminoethyl)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 $[Cd_2L](ClO_4)_2{\cdot}2CH_3OH$ which had precipitated were filtered off, washed with methanol and dried *in vacuo*, with a yield of 65%. *Anal.* Calc. for $C_{30}H_{44}N_8O_{12}Cl_2Br_2Cd_2$(%): C, 30.96; H, 3.82; N, 9.62; Cd, 19.42. Found: C, 31.05; H, 3.81; N, 9.60; Cd, 19.12. IR (cm^{-1}): 3410 (br, $\nu_{(OH)}CH_3OH$); 3295, 3348 (s, $\nu_{(NH2)}$); 1637 (s, $\nu_{(C=N)}$); 1550 (s, $\nu_{(Ph\text{-}O)}$); 1106 (s, $\nu_{(ClO4-)}$). UV-Vis (λ_{max}(nm), CH_3CN): 384 (8678 M cm^{-1}); 240 (27119); 220(30729). Λ_M (CH_3CN, 279K): 250 S cm^2 mol^{-1}. Yellowish crystals of $[Cd_2L](ClO_4)_2{\cdot}0.5CH_3OH$ suitable for 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 $[Cd_2L](ClO_4)_2{\cdot}0.5CH_3OH$ are summarized in Table I. Diffraction data were collected on a Siemens P_4 diffractometer equipped with graphite-monochromated MoK_α radiation (λ = 0.71073 Å) over the range $2° < 2\theta < 48°$, with a ω-2θ scan mode and with a ω scan width of 1.65°, scan rate 7° min^{-1}. The structure was solved by direct methods using programs contained in the SHELXTL package. Remaining non-hydrogen atoms were located in a difference Fourier map. Hydrogen atoms were introduced in calculated positions and refined. All calculations were performed using the programs contained in the SHELXTL package.

RESULTS AND DISCUSSION

Spectroscopic Characterization of the Binuclear Complex

In the infrared spectrum a strong peak at 1637 cm^{-1} corresponds to the C=N stretch. Symmetric and asymmetric stretching frequencies (3295 and 3348 cm^{-1})

TABLE I Crystal data and collection parameters for the complex.

Formula	$C_{28.5}H_{36}N_8O_{10.5}Cl_2Br_2Cd_2$
Molecular weight	1116.2
Colour	yellowish
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	11.633(15)
b (Å)	16.370(2)
c (Å)	21.193(2)
β (deg)	96.12(12)
V (Å^3)	4013.0(8)
Z	4
D_c (g cm^{-3})	1.84
$F(000)$	2180
μ (cm^{-1})	32.46
Crystal dimensions (mm)	0.26 × 0.28 × 0.32
Radiation (Å)	MoK_α (0.71073)
Scan mode	ω-2θ
2θ range (deg)	2 to 48
No. reflections measured	6192
No. reflections used ($F > 6.0\sigma(F)$)	3181
w^{-1}	$\sigma^2(F) + 0.008F^2$
Final R, R_w	0.049, 0.069

for NH_2 groups are also present, but no strong peaks at 1650 ~ 1700 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 3410 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. Some CH_3OH molecules are lost during growth of single crystals of $[Cd_2L](ClO_4)_2$ for the X-ray structure determination. The strong peak at 1106 cm^{-1} indicates that ClO_4^- does not take part in coordination with Cd(II). This is also confirmed by the molar conductivity of the complex which is characteristic of a 2:1 electrolyte; [11] thus the phenoxy oxygens are also coordinated to cadmium(II). The three strong peaks in the UV region of the electronic spectrum are assigned to π-π^* transitions of benzene rings and C=N groups. [12]

Description of the Structure of $[Cd_2L](ClO_4)_2 \cdot 0.5CH_3OH$

A perspective view of the $[Cd_2L]^{2+}$ cation is shown in Figure 1. Coordinates of non-hydrogen atoms and selected bond distances and angles are given in Tables II and III, respectively. In Figure 1 it is seen that each Cd(II) atom is enclosed within the polyaza macrocycle. Each is coordinated by one bridgehead nitrogen atom, two imino nitrogen atoms, one amine nitrogen atom of the pendant arms and two oxygen atoms of phenoxy groups. Each of two oxygen atoms of phenoxy groups bridges the two cadmium atoms. Cd(II) lies in an N_4O_2 coordination environment which takes the form of a capped trigonal bipyramid (Figure 2). For Cd(1), the amino nitrogen N(3) and imino nitrogens N(1) and N(4) occupy equatorial positions, and one phenoxy oxygen O(1) deviates from the equatorial plane; the tertiary nitrogen N(2) and another phenoxy oxygen O(2) occupy approximately axial positions. For Cd(2), the amino nitrogen N(7) and imino nitrogens N(5) and N(8) occupy equatorial positions and one phenoxy oxygen O(2) deviates from the equatorial plane; the tertiary nitrogen N(6) and another phenoxy oxygen O(1) occupy approximately axial positions. The dihedral angle between plane 1 (Cd(1), O(1), Cd(2)) and plane 2 (Cd(1), O(2), Cd(2)) is 49.3°. Cd-O distances are in the range 2.313 ~ 2.338Å, being normal coordination bonds. The Cd-N (imino) distances are in the range 2.25 ~ 2.27Å, being approximately equal. Cd-N bonds are shorter than standard Cd-N bond distances of 2.33 ± 0.005 Å. [13] This means that the ligand is strongly coordinated to Cd(II). Conversely, distances between cadmium(II) and the tertiary nitrogens are *ca* 2.54 Å, implying that the tertiary nitrogens coordinate weakly. The long

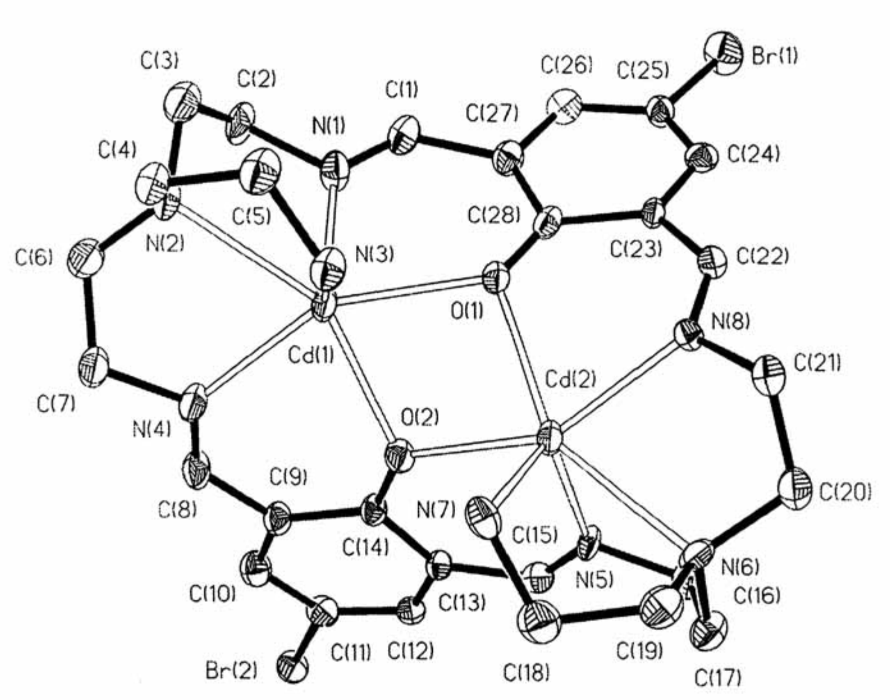


FIGURE 1 Perspective view of the complex showing the atom labelling scheme.

TABLE II Positional parameters for the complex ($\times 10^4$).

Atom	*x/a*	*y/b*	*z/c*	*U(eq)*
Cd(1)	1233(1)	2990(1)	1718(1)	45(1)
Cd(2)	3846(1)	3981(1)	2245(1)	39(1)
Br(1)	6186(1)	1013(1)	11(1)	76(1)
Br(2)	2669(1)	821(1)	4866(1)	52(1)
O(1)	3086(2)	3161(2)	1409(2)	42(1)
O(2)	2509(2)	3128(2)	2642(2)	42(1)
N(1)	1283(2)	1980(2)	999(2)	53(1)
N(3)	795(1)	4246(2)	1276(2)	56(1)
N(2)	783(2)	2844(2)	1166(2)	48(1)
N(4)	65(2)	2763(2)	2491(2)	46(1)
N(5)	4947(2)	3397(2)	3061(2)	38(1)
N(6)	5349(7)	5043(2)	2661(2)	46(1)
N(7)	2823(1)	5088(2)	2511(2)	59(1)
N(8)	4964(2)	4305(2)	1454(2)	36(1)
C(1)	2117(2)	1659(2)	755(2)	53(1)
C(2)	133(2)	1579(2)	812(2)	59(1)
C(3)	−737(2)	2258(2)	634(2)	64(1)
C(5)	−153(2)	4151(2)	747(2)	60(1)
C(4)	−1142(2)	3646(2)	958(2)	52(1)
C(6)	−1483(2)	2509(2)	1655(2)	64(1)
C(7)	−1179(2)	2845(2)	2297(2)	54(1)
C(8)	368(2)	2440(2)	3009(2)	51(1)
C(9)	1515(2)	2303(2)	3338(2)	45(1)
C(10)	1568(2)	1770(2)	3854(2)	52(1)
C(11)	2613(2)	1592(2)	4189(2)	47(1)
C(12)	3603(2)	1968(2)	4031(2)	38(1)
C(13)	3589(2)	2489(2)	3535(2)	33(1)
C(14)	2539(2)	2665(2)	3133(2)	37(1)
C(15)	4677(2)	2902(2)	3460(2)	44(1)
C(16)	6091(2)	3775(2)	3159(2)	53(1)
C(17)	6953(2)	4697(2)	3241(2)	54(1)
C(18)	3523(2)	5531(2)	3007(2)	65(1)
C(19)	4675(2)	5795(2)	2791(2)	61(1)
C(20)	6131(2)	5219(2)	2149(2)	54(1)
C(21)	5537(2)	5106(2)	1504(2)	47(1)
C(22)	5268(2)	3813(2)	1059(2)	42(1)
C(23)	4841(2)	2988(2)	905(2)	34(1)
C(24)	5511(2)	2468(2)	575(2)	42(1)
C(25)	5215(2)	1724(2)	391(2)	42(1)
C(26)	4088(2)	1480(2)	462(2)	51(1)
C(27)	3349(2)	1964(2)	786(2)	45(1)
C(28)	3719(2)	2726(2)	1079(2)	41(1)

*Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE III Selected bond distances (Å) and angles (°) for the complex.

Cd(1)-O(1)	2.335(2)	Cd(1)-O(2)	2.338(3)
Cd(1)-N(1)	2.253(3)	Cd(1)-N(3)	2.295(3)
Cd(1)-N(2)	2.518(2)	Cd(1)-N(4)	2.267(3)
Cd(2)-O(1)	2.320(3)	Cd(2)-O(2)	2.313(3)
Cd(2)-N(5)	2.251(3)	Cd(2)-N(6)	2.556(3)
Cd(2)-N(7)	2.273(3)	Cd(2)-N(8)	2.292(3)
O(1)-Cd(1)-O(2)	72.6(1)	O(1)-Cd(1)-N(1)	78.9(1)
O(2)-Cd(1)-N(1)	125.3(1)	O(1)-Cd(1)-N(3)	87.1(1)
O(2)-Cd(1)-N(3)	110.4(1)	N(1)-Cd(1)-N(3)	113.7(1)
O(1)-Cd(1)-N(2)	136.3(1)	O(2)-Cd(1)-N(2)	151.0(1)
N(1)-Cd(1)-N(2)	72.9(1)	N(3)-Cd(1)-N(2)	74.9(1)
O(1)-Cd(1)-N(4)	149.8(1)	O(2)-Cd(1)-N(4)	77.7(1)
N(1)-Cd(1)-N(4)	115.4(1)	N(3)-Cd(1)-N(4)	108.5(1)
N(2)-Cd(1)-N(4)	73.7(1)	O(1)-Cd(2)-O(2)	73.3(1)
O(1)-Cd(2)-N(5)	118.7(1)	O(2)-Cd(2)-N(5)	79.3(1)
O(1)-Cd(2)-N(6)	148.0(1)	O(2)-Cd(2)-N(6)	138.3(1)
N(5)-Cd(2)-N(6)	73.3(1)	O(1)-Cd(2)-N(7)	118.9(1)
O(2)-Cd(2)-N(7)	90.1(1)	N(5)-Cd(2)-N(7)	114.7(1)
N(6)-Cd(2)-N(7)	74.2(1)	O(1)-Cd(2)-N(8)	77.0(1)
O(2)-Cd(2)-N(8)	149.5(1)	N(5)-Cd(2)-N(8)	109.8(1)
N(6)-Cd(2)-N(8)	70.9(1)	N(7)-Cd(2)-N(8)	110.5(1)
Cd(1)-O(1)-Cd(2)	98.3(1)	Cd(1)-O(2)-Cd(2)	98.4(1)
Cd(2)-O(1)-C(28)	122.8(2)	Cd(1)-O(1)-C(28)	133.3(2)

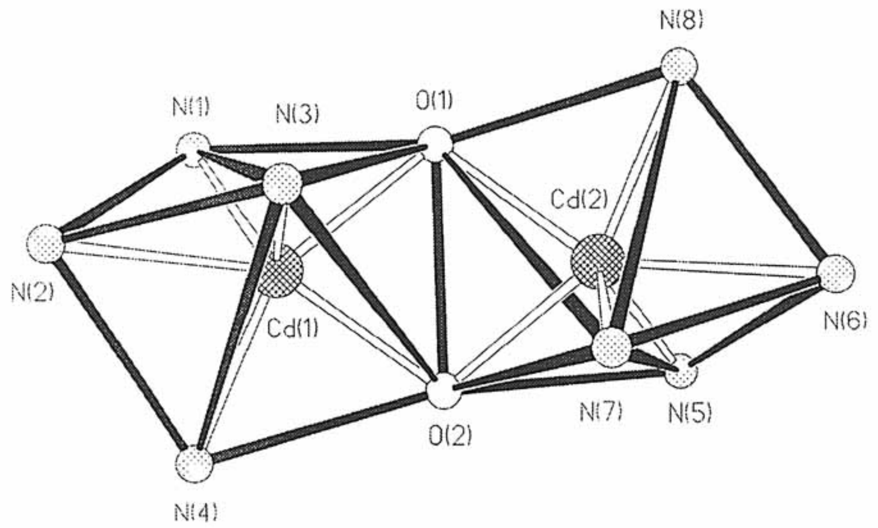


FIGURE 2 Coordination environments of the central cadmium ions.

Cd...Cd distance (3.521Å) indicates that there is no interaction between the two metal atoms. N(2)-N(6) is 6.80Å, being much shorter than corresponding distance of 9.01Å in the cryptate. [7] Cd(1) is similar to Cd(2) in coordination environment but slightly different to Cd(2) in distortion of geometry. An analogous complex, $[Cu_2L'(OH)](ClO_4)_3$, which was synthesized by [2 + 2] Schiff-base condensation of *tris*(2-aminoethyl)amine (tren) with isophthalic aldehyde in the presence of $Cu(ClO_4)_2{\cdot}6H_2O$ is unstable. [14] In our work, the phenoxy oxygen atoms bridging the two Cd(II) ions enhance the stability of the complex and it is more stable than its analogue $[Cu_2L'(OH)](ClO_4)_3$.

Supplementary Material

Lists of observed and calculated structure factors, bond distances and angles, anisotropic thermal parameters for non-hydrogen atoms, atomic positions for hydrogen atoms and a packing diagram of the complex are available from the authors on request.

Acknowledgements

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