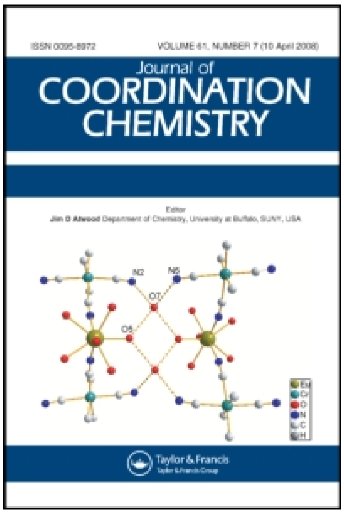

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# SYNTHESIS AND STRUCTURE OF A NEW BINUCLEAR CADMIUM(II) CRYPTATE

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# SYNTHESIS AND STRUCTURE OF A NEW BINUCLEAR CADMIUM(II) CRYPTATE

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A new binuclear cadmium(II) cryptate has been synthesized by [2+3] Schiff base condensation of *tris*(3-aminoethyl)amine (tren) with sodium 2,6-diformyl-4-chlorophenolate in the presence of $Cd(ClO_4)_2 \cdot 6H_2O$. The crystal structure shows that two cadmium(II) ions are bridged by three $\mu_2$-phenoxy oxygen atoms. Each cadmium(II) is located in a capped triangular prismatic coordination environment ($N_4O_3$).

*Keywords:* Binuclear; cadmium(II) complex; cryptate; oxygen bridge; crystal structure; capped trigonal prism

## INTRODUCTION

We have reported a series of polyaza cryptands which contain strong donors, namely phenoxy oxygen atoms as well as amine nitrogen atoms.[1–3] These are excellent for catalysis and biological simulation because of the nature of the ligands.[4,5]

Cadmium(II) is an environmental pollutant which inhibits RNA polymerase activity *in vivo*[6,7] and reacts readily with proteins and other biological molecules. The macrocyclic chemistry of cadmium has been developed recently,[8] but only a few crystal structures have been reported, especially for

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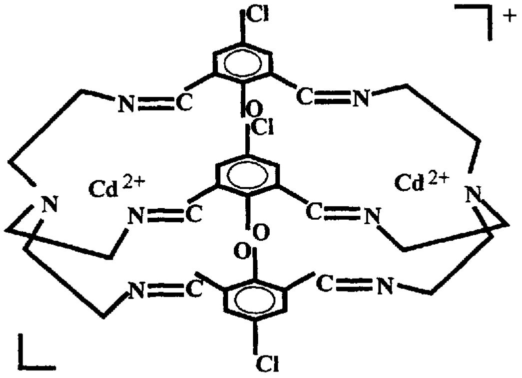

FIGURE 1 The structure of the cryptate cation $[Cd_2(H_{-3}L)]^+$.

binuclear cadmium cryptates.[1,3,5] In this paper, we report the synthesis, characterization and X-ray crystal structure of a new $\mu_2$-oxo bridged binuclear cadmium(II) cryptate as shown in Figure 1.

## EXPERIMENTAL

### Materials

2,6-Diformyl-4-chlorophenol was prepared by a literature method.[9,10] Sodium 2,6-diformyl-4-chlorophenolate was obtained by mixing equimolar amounts of 2,6-diformyl-4-chlorophenol and NaOH in ethanol. *Tris*(3-aminoethyl)amine was used as purchased without further treatment.

### Physical Measurements

Solution electrical conductivity was measured by a BDS-A conductometer (Jiangsu, China) with solution concentrations of $\sim 10^{-4}$ mol dm$^{-3}$ in acetonitrile. IR spectra were measured using KBr discs with a Nicolet 5DX FT-IR spectrophotometer. Electronic spectra were recorded on a Shimadzu UV-240 spectrophotometer.

### Preparation of the Cryptate $[Cd_2(H_{-3}L)](ClO_4) \cdot 0.25H_2O$

To a stirred solution of sodium 2,6-diformyl-4-chlorophenolate (0.155 g, 0.75 mmol) and $Cd(ClO_4) \cdot 6H_2O$ (0.2621 g, 0.63 mmol) in 30 cm$^3$ of absolute methanol wàs added dropwise a solution of *tris*(3-aminoethyl)amine (0.073 g, 0.5 mmol) in 15 $cm^3$ of absolute methanol at 0°C. After stirring for 2 h at 35°C, the yellowish microcrystals which precipitated were filtered off, washed with methanol and dried *in vacuo* (yield 75%). *Anal.*, found: C, 40.3; H, 3.6; N, 10.1; Cd, 20.6. Calcd. for $C_{36}H_{38}N_8O_8Cl_4Cd_2$ (%): C, 40.1; H, 3.6; N, 10.4; Cd, 20.9%. IR ($cm^{-1}$, KBr): 3455br, $\nu_{(OH)}(H_2O)$; 1634s, $\nu_{(C=N)}$; 1540s, $\nu_{(Ar-O)}$; 1103s, $\nu_{(ClO_4^-)}$. Electronic spectrum ($\lambda_{max}$(nm), $CH_3CN$): 240 (10 990 $M^{-1}cm^{-1}$); 410 (3754). $\Lambda_M$ ($CH_3CN$, 291 K): 104 S $cm^2 mol^{-1}$. Yellowish crystals of $[Cd_2(H_{-3}L)](ClO_4) \cdot 0.25H_2O$ suitable for X-ray structure determination were obtained by slow evaporation of the mother liquor at ambient 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.

## Structure Determination of $[Cd_2(H_{-3}L)](ClO_4) \cdot 0.25H_2O$

*Crystal data*: $C_{36}H_{36.50}N_8O_{7.25}Cl_4Cd_2$, $M = 1063.83$, yellowish plates, monoclinic, space group $C2/c$, $a = 18.970(4)$, $b = 19.988(3)$, $c = 21.900(5)$ Å, $\beta = 100.06(3)°$, $V = 8177(3)$ Å$^3$, $Z = 8$, $F(000) = 4244$, $Dc = 1.73$ g $cm^{-3}$, $T = 296$ K, $\mu = 13.60$ $cm^{-1}$.

## Data Collection and Refinement

A single crystal of dimensions 0.24 × 0.35 × 0.44 mm was mounted on a glass fibre. The crystal data were collected on a Enraf-Nonius CAD4 four-circle diffractometer with graphite-monochromated MoK$\alpha$ radiation ($\lambda = 0.71073$ Å) using an $\omega$–$2\theta$ scan mode wih $\omega$ scan width $0.50 + 0.350 \tan\theta$, scan rate $< 5.49°$ $min^{-1}$. A total of 6667 independent reflections was collected in the range $3.6° < 2\theta < 45°$, of which 3347 reflections with $I > 2\sigma(I)$ were used in the structure determination and refinement after Lp correction. The structure was solved by direct methods. Remaining non-hydrogen atoms were located from a difference Fourier map. Hydrogen atoms were introduced in calculated positions but not refined. The final least-square cycle gave $R = 0.050$, $R_w = 0.134$ ($w = 1/\sigma^2(F)$). The maximum and minimum residuals were 0.71 and $-0.65$ e Å$^{-3}$ respectively. All calculations were performed using the programs contained in the TEXSAN package.

## RESULTS AND DISCUSSION

In the infrared spectrum a strong peak appears at *ca.* 1634 $cm^{-1}$ corresponding to the imino C=N band; the IR spectrum showed no stretching frequencies for $NH_2$ groups, nor for carbonyl groups. This means that all the $NH_2$ and CO groups have been condensed into C=N bonds. A broad band at *ca.* 3455 $cm^{-1}$ characteristic of the OH group of $H_2O$ showed that $H_2O$ molecules exist in the cryptate, being in agreement with the elemental analysis. Part of the $H_2O$ molecule was lost during data collection. The strong single peak at *ca.* 1103 $cm^{-1}$ without splitting shows that $ClO_4^-$ does not take part in coordination with the Cd(II) atom. This was confirmed by the molar conductivity of the cryptate ($\Lambda_M$ is 104 $S\,cm^2\,mol^{-1}$) attributable to a 1 : 1 electrolyte.[11] There are two intense absorptions in the electronic spectrum of the cryptate which are assigned to $\pi-\pi^*$ transitions of the K band of the benzene rings and of C=N groups.

A perspective view of the cation $[Cd_2(H_{-3}L)]^+$ and a packing diagram is shown in Figure 2. The selected bond distances and bond angles are given in Tables I and II, respectively; final atomic coordinates are listed in Table III.

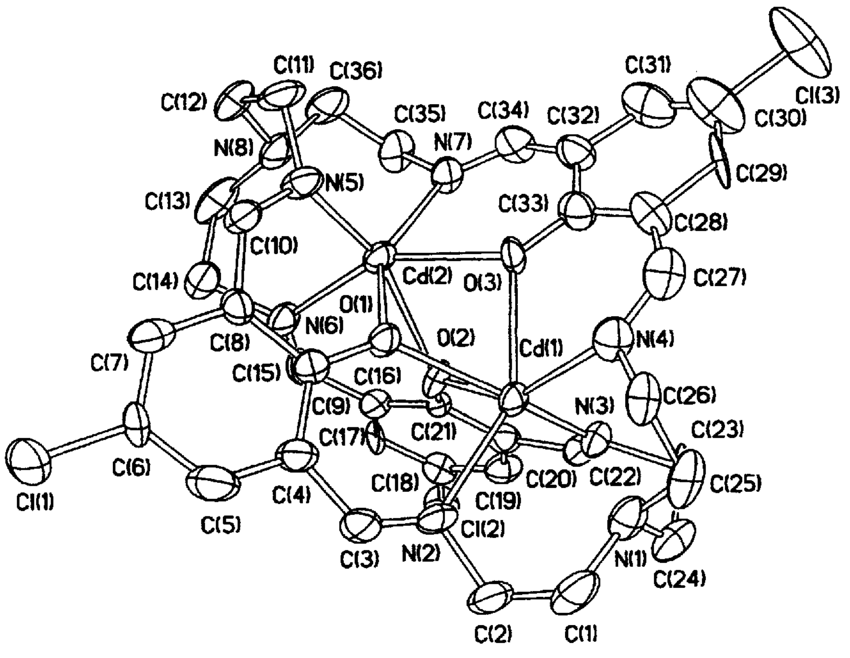

FIGURE 2 A perspective view of the cation $[Cd_2(H_{-3}L)]^+$.

TABLE I Selected bond distances (Å) for the cryptate $[Cd_2(H_{-3}L)](ClO_4) \cdot 0.25H_2O$

| | | | |
|---|---|---|---|
| Cd(1)–N(4) | 2.298(4) | Cd(1)–O(1) | 2.311(2) |
| Cd(1)–O(2) | 2.328(3) | Cd(1)–N(3) | 2.330(3) |
| Cd(1)–N(2) | 2.336(3) | Cd(1)–O(3) | 2.383(2) |
| Cd(2)–N(5) | 2.291(2) | Cd(2)–O(3) | 2.297(3) |
| Cd(2)–O(2) | 2.315(2) | Cd(2)–N(7) | 2.321(3) |
| Cd(2)–N(6) | 2.322(4) | Cd(1)–O(1) | 2.385(2) |

TABLE II Selected bond angles (°) for the cryptate $[Cd_2(H_{-3}L)](ClO_4) \cdot 0.25H_2O$

| | | | |
|---|---|---|---|
| N(4)–Cd(1)–O(1) | 102.22(9) | N(4)–Cd(1)–O(2) | 145.63(9) |
| O(1)–Cd(1)–O(2) | 73.18(8) | N(4)–Cd(1)–N(3) | 102.09(11) |
| O(1)–Cd(1)–N(3) | 148.78(10) | O(2)–Cd(1)–N(3) | 75.68(11) |
| N(4)–Cd(1)–N(2) | 115.55(11) | O(1)–Cd(1)–N(2) | 77.32(8) |
| O(2)–Cd(1)–N(2) | 96.99(11) | N(3)–Cd(1)–N(2) | 108.99(9) |
| N(4)–Cd(1)–O(3) | 74.76(10) | O(1)–Cd(1)–O(3) | 70.25(7) |
| O(2)–Cd(1)–O(3) | 71.67(8) | N(3)–Cd(1)–O(3) | 97.82(8) |
| N(2)–Cd(1)–O(3) | 147.48(9) | N(4)–Cd(1)–Cd(2) | 111.44(7) |
| O(1)–Cd(1)–Cd(2) | 43.81(5) | O(2)–Cd(1)–Cd(2) | 42.10(5) |
| N(3)–Cd(1)–Cd(2) | 108.24(8) | N(2)–Cd(1)–Cd(2) | 110.03(8) |
| O(3)–Cd(1)–Cd(2) | 41.79(8) | N(5)–Cd(2)–O(3) | 103.33(11) |
| N(5)–Cd(2)–O(2) | 144.87(9) | O(3)–Cd(2)–O(2) | 73.45(9) |
| N(5)–Cd(2)–N(7) | 111.71(8) | O(3)–Cd(2)–N(7) | 76.94(11) |
| O(2)–Cd(2)–N(7) | 101.74(9) | N(5)–Cd(2)–N(6) | 104.41(11) |
| O(3)–Cd(2)–N(6) | 148.76(8) | O(2)–Cd(2)–N(6) | 75.62(10) |
| N(7)–Cd(2)–N(6) | 105.43(11) | N(5)–Cd(2)–O(1) | 74.01(8) |
| O(3)–Cd(2)–O(1) | 70.44(8) | O(2)–Cd(2)–O(1) | 72.05(8) |
| N(7)–Cd(2)–O(1) | 147.25(11) | N(6)–Cd(2)–O(1) | 103.97(9) |
| N(5)–Cd(2)–Cd(1) | 111.49(8) | O(3)–Cd(2)–Cd(1) | 43.73(5) |
| O(2)–Cd(2)–Cd(1) | 42.38(8) | N(7)–Cd(2)–Cd(1) | 112.06(8) |
| N(6)–Cd(2)–Cd(1) | 111.32(6) | O(1)–Cd(2)–Cd(1) | 42.12(5) |
| Cd(2)–O(3)–Cd(1) | 94.48(9) | Cd(2)–O(3)–Cd(1) | 95.51(9) |
| C(9)–O(1)–Cd(1) | 135.8(2) | C(9)–O(1)–Cd(2) | 118.8(2) |
| Cd(1)–O(1)–Cd(2) | 94.07(5) | C(21)–O(2)–Cd(2) | 126.4(2) |
| C(21)–O(2)–Cd(1) | 135.5(2) | Cd(2)–O(2)–Cd(1) | 95.51(2) |
| C(33)–O(3)–Cd(2) | 136.3(2) | C(33)–O(3)–Cd(1) | 125.9(2) |
| C(26)–N(4)–Cd(1) | 112.8(2) | C(27)–N(4)–Cd(1) | 129.6(3) |
| C(10)–N(5)–Cd(2) | 123.0(2) | C(11)–N(5)–Cd(2) | 114.9(2) |
| C(14)–N(6)–Cd(2) | 115.1(2) | C(15)–N(6)–Cd(2) | 125.4(3) |

It may be seen from Figure 2 that the complex cation has no crystallographic $C_2$ symmetry. Each cadmium atom is located at the centre of a capped triangular prism with coordination number seven. Around the Cd(1) centre, three imino nitrogen atoms, N(2), N(3), N(4), form one plane of the trigonal prism, and three phenoxy oxygen atoms, O(1), O(2), O(3), the other. The dihedral angle between the faces is 2.4°. Cd is located at the centre of the two planes and the bridgehead nitrogen is located in the capped position. Thus the coordination environment of Cd(1) atom may be considered as a capped triangular prism. Cd(2) is similar. Cd(1)–N(imino)

TABLE III Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [Å$^2 \times 10^3$] for the complex. $U(eq)$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor

| | *x/a* | *y/b* | *z/c* | *U(eq)* |
|---|---|---|---|---|
| Cd(1) | 6430(1) | 6039(1) | 655(1) | 48(1) |
| Cd(2) | 5119(1) | 7203(1) | 748(1) | 49(1) |
| Cl(1) | 5982(1) | 8377(1) | −2191(1) | 122(1) |
| Cl(2) | 8023(1) | 8377(1) | 3292(1) | 80(1) |
| Cl(3) | 3889(1) | 4024(1) | 2190(1) | 191(1) |
| O(1) | 5703(1) | 6731(1) | −31(1) | 51(1) |
| O(2) | 6309(1) | 7035(2) | 1179(1) | 69(1) |
| O(3) | 5259(1) | 6072(1) | 910(1) | 55(1) |
| N(1) | 7456(1) | 5117(2) | 612(1) | 69(1) |
| N(2) | 7214(1) | 6443(2) | 28(1) | 65(1) |
| N(3) | 7066(1) | 5855(2) | 1650(1) | 55(1) |
| N(4) | 5948(1) | 5002(2) | 393(1) | 68(1) |
| N(5) | 4313(1) | 7267(2) | −160(1) | 61(1) |
| N(6) | 5595(1) | 8274(2) | 888(1) | 56(1) |
| N(7) | 4556(1) | 7015(2) | 1592(1) | 58(1) |
| N(8) | 4071(1) | 8133(2) | 791(1) | 65(1) |
| C(1) | 7901(2) | 5389(3) | 182(2) | 88(2) |
| C(2) | 7931(2) | 6136(3) | 211(2) | 84(2) |
| C(3) | 7098(2) | 6806(3) | −449(1) | 68(2) |
| C(4) | 6440(1) | 7127(3) | −727(2) | 70(2) |
| C(5) | 6484(2) | 7493(3) | −1249(2) | 85(2) |
| C(6) | 5902(2) | 7885(3) | −1568(2) | 71(2) |
| C(7) | 5250(2) | 7841(3) | −1365(2) | 87(2) |
| C(8) | 5177(1) | 7449(2) | −844(1) | 51(1) |
| C(9) | 5781(1) | 7090(2) | −495(1) | 48(1) |
| C(10) | 4481(1) | 7465(2) | −667(2) | 56(1) |
| C(11) | 3563(1) | 7440(2) | −87(2) | 80(2) |
| C(12) | 3550(2) | 8092(2) | 218(2) | 70(2) |
| C(13) | 4448(2) | 8810(2) | 858(2) | 83(2) |
| C(14) | 5120(2) | 8819(3) | 587(2) | 73(2) |
| C(15) | 6110(2) | 8445(2) | 1306(2) | 64(2) |
| C(16) | 6611(1) | 8000(1) | 1736(1) | 53(1) |
| C(17) | 7041(1) | 8346(2) | 2223(1) | 51(1) |
| C(18) | 7496(1) | 7988(1) | 2672(1) | 56(2) |
| C(19) | 7518(1) | 7298(1) | 2620(1) | 62(2) |
| C(20) | 7111(1) | 6975(2) | 2108(1) | 56(1) |
| C(21) | 6641(1) | 7312(1) | 1640(1) | 31(1) |
| C(22) | 7261(1) | 6247(2) | 2097(1) | 54(1) |
| C(23) | 7368(2) | 5166(2) | 1718(2) | 56(2) |
| C(24) | 7845(2) | 5049(3) | 1236(2) | 84(2) |
| C(25) | 7104(2) | 4503(3) | 369(2) | 79(2) |
| C(26) | 6363(2) | 4616(3) | 11(2) | 70(2) |
| C(27) | 5507(2) | 4656(3) | 647(2) | 79(2) |
| C(28) | 5069(2) | 4923(3) | 1077(2) | 74(2) |
| C(29) | 4735(2) | 4461(3) | 1392(2) | 81(2) |
| C(30) | 4300(2) | 4617(4) | 1792(2) | 125(3) |
| C(31) | 4217(2) | 5253(4) | 1925(2) | 107(2) |
| C(32) | 4521(2) | 5802(3) | 1635(2) | 68(2) |
| C(33) | 4980(2) | 5620(3) | 1213(2) | 66(2) |
| C(34) | 4384(2) | 6454(3) | 1805(2) | 70(2) |
| C(35) | 4294(2) | 7639(3) | 1829(2) | 72(2) |

TABLE III (*Continued*)

| | $x/a$ | $y/b$ | $z/c$ | $U(eq)$ |
|---|---|---|---|---|
| C(36) | 3755(2) | 7956(2) | 1322(2) | 81(2) |
| Cl(4) | 3480(1) | 9382(1) | −1275(1) | 174(1) |
| O(41) | 3879(2) | 9582(2) | −702(1) | 179(2) |
| O(42) | 3670(2) | 8751(2) | −1498(2) | 132(3) |
| O(43) | 2734(1) | 9318(4) | −1219(3) | 216(5) |
| O(44) | 3546(3) | 9853(2) | −1749(2) | 245(6) |
| O(42′) | 3017(2) | 9918(2) | −1519(3) | 184(4) |
| O(43′) | 3984(2) | 9276(4) | −1678(2) | 293(7) |
| O(44′) | 3054(2) | 8804(2) | −1243(4) | 433(12) |
| O(1w) | 5000 | 9673(12) | 2500 | 252(8) |

distances are in the range 2.30–2.33 Å. Cd(1)–O bond distances are in the range 2.31–2.38 Å. These are close to those in the case of the ligand formed by condensation of tren with 2,6-diformyl-4-methylphenol.[5] The Cd(1)–N(1) (bridgehead nitrogen) bond distance is *ca* 2.70 Å, implying a weak interaction. It is shorter than those in the related cadmium cryptate synthesized by condensation of tren and dmp, the corresponding distance being *ca* 2.79 Å. In addition, the distance between Cd(1) and Cd(2), 4.42 Å, is larger than that in the corresponding cryptate involving tren (3.44 Å), but the distance between bridgehead nitrogens, 8.87 Å, is shorter (9.01 Å). This is due to the effect of the substituent. Replacement of the methyl group in the benzene ring by a chloro atom causes transformation of the seven-coordinate capped octahedron into the triangular prism.

### *Acknowledgements*

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### *Supplementary Material*

Full lists of crystallographic data are available from the authors upon request.

### *References*

[1] X.Y. Xu, J.L. Chen, Q.H. Luo and M.C. Shen, *Polyhedron*, **16**, 223 (1997).

[2] J. Wang, Q.H. Luo, M.C. Shen, X.Y. Huang and Q.J. Wu, *J. Chem. Soc., Chem. Commun.*, 2373 (1995).

[3] X.Y. Xu, J.L. Chen, Q.H. Luo and M.C. Shen, *Polyhedron*, **16**, 1301 (1997).

[4] P.A. Vigato, S. Tamburini and D.E. Fenton, *Coord. Chem. Rev.*, **106**, 105 (1990).

[5] M.G.B. Drew, O.W. Howarth, G.G. Morgan and J. Nelson, *J. Chem. Soc., Dalton Trans.*, 3149 (1994).

[6] K.B. Jacobson and J.E. Turner, *Toxicology*, **60**, 1 (1980).
[7] H.A. Hidalgo, V. Koppa and E.S. Bryan, *FEBS Lett.*, **64**, 159 (1976).
[8] D. Dakternicks, *Coord. Chem. Rev.*, **98**, 288 (1990).
[9] X.Y. Xu, Q.H. Luo and M.C. Shen, *Polyhedron*, **16**, 915 (1997).
[10] S. Taniguchi, *Bull. Chem. Soc. Jpn.*, **57**, 268 (1984).
[11] W.J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).