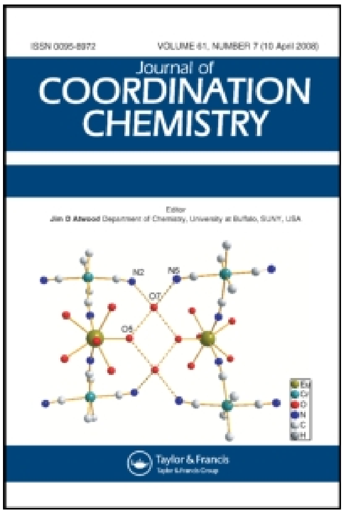

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis and Crystal Structure of an Azido-Bridged Cadmium(II) Dimer $[L_2Cd_2(\mu\text{-}N_3)_2(N_3)_2]$ (L=1,4,7-Triazacyclononane)

Wen Gu[a]; Cheng-Zhi Xie[a]; He-Dong Bian[a]; Peng Chen[a]; Shi-Ping Yan[a]; Dai-Zheng Liao[a]; Zong-Hui Jiang[a]
[a] Department of Chemistry, Nankai University, Tianjin, P.R. China

To cite this Article Gu, Wen , Xie, Cheng-Zhi , Bian, He-Dong , Chen, Peng , Yan, Shi-Ping , Liao, Dai-Zheng and Jiang, Zong-Hui(2003) 'Synthesis and Crystal Structure of an Azido-Bridged Cadmium(II) Dimer $[L_2Cd_2(\mu\text{-}N_3)_2(N_3)_2]$ (L=1,4,7-Triazacyclononane)', Journal of Coordination Chemistry, 56: 5, 427 — 431

To link to this Article: DOI: 10.1080/0095897031000092359

URL: http://dx.doi.org/10.1080/0095897031000092359

J. Coord. Chem., 2003, Vol. 56, No. 5, pp. 427–431

Taylor & Francis
Taylor & Francis Group

SYNTHESIS AND CRYSTAL STRUCTURE OF AN AZIDO-BRIDGED CADMIUM(II) DIMER $[L_2Cd_2(\mu\text{-}N_3)_2(N_3)_2]$ (L=1,4,7-TRIAZACYCLONONANE)

WEN GU, CHENG-ZHI XIE, HE-DONG BIAN, PENG CHEN,
SHI-PING YAN*, DAI-ZHENG LIAO and ZONG-HUI JIANG

Department of Chemistry, Nankai University, Tianjin, 300071, P.R. China

(Received 12 September 2002)

A new dinuclear Cd(II) complex, $[L_2Cd_2(\mu\text{-}N_3)_2(N_3)_2]$, containing two end-on bridging azide ligands, two monodentate N_3 ligands and 1,4,7-triazacyclononane as the capping ligand, has been synthesized and its structure determined by X-ray crystallography. The complex crystallizes in the monoclinic space group $P2_1/c$ with $a = 8.467(3)$, $b = 14.359(5)$, $c = 10.115(4)$Å, $\beta = 95.026(6)°$ and $z = 4$. The cadmium(II) centre is six-coordinate with distorted octahedral geometry, bonded to three N atoms of the 1,4,7-triazacyclononane, two nitrogen atoms of μ-azide bridges and one nitrogen atom of a monodentate azide ligand. Neighboring Cd(II) atoms are linked by the double end-on azide bridges.

Keywords: Cd(II); Azido complex; Crystal structure; Triazamacrocycle

INTRODUCTION

The extent studies concerning azido-bridged compounds is large [1]. One of reasons for this is that the azide ion as a versatile ligand and can coordinate to metal ions in a variety of modes. In addition to monodentate behaviour, the azide ion can act as a bridging ligand either in the end-to-end ($\mu_{1,3}$-N_3) or in the end-on ($\mu_{1,1}$-N_3) mode to yield di- and polynuclear complexes [2]. Combinations of $\mu_{1,3}$-azide and terminal azide are more common in some transition metals complexes, for example with copper [3,4] and nickel [5–7], but they are rare for cadmium. Here we report the synthesis and crystal structure of a new cadmium complex $[L_2Cd_2(\mu\text{-}N_3)_2(N_3)_2]$, where L is 1,4,7-triazacyclononane. The ligand L is expected to coordinate facially in octahedral complexes.

---

*Corresponding author.

ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/0095897031000092359

EXPERIMENTAL

Materials and Physical Measurements

Elemental analyses were determined on a Perkin-Elmer 240 instrument. IR spectra were measured as KBr pellets on a Shimadzu 408 spectrophotometer in the range 200–4000 cm^{-1}. All reagents were commercially available and the macrocyclic ligand 1,4,7-triazacyclononane was prepared as described in the literature [8].

Preparation of the Complex

To a stirred solution of $Cd(NO_3)_2$ (0.2 mmol) in 10 ml of methanol was added drop by drop a solution of 1,4,7-triazacyclononane (0.2 mmol). After stirring for 0.5 h, a solution of NaN_3 (0.4 mmol) in 10 ml of methanol was added drop by drop. The white mixture was stirred continually for *ca* 2 h, during which time a white solid precipitated. This was filtered off, washed with methanol and air-dried. The product was recrystallized from CH_3OH–CH_3CN–H_2O (4 : 1 : 1), yield 70%. Suitable colourless crystals were obtained by slow evaporation of the solution. *Anal.* Found: C, 21.7; H; 4.45; N, 38.2. Calcd. For $C_{12}H_{30}Cd_2N_{18}$ (%): C, 22.1; H, 4.61; N, 38.7. The occurrence in the IR spectrum of two strong peaks at 2037 and 2079 cm^{-1}, corresponding to $\nu_{as}(N_3)$ stretching vibrations, suggests the presence of different types of azide ligand.

Crystal Structure Determination and Refinement

A colourless crystal (0.25 × 0.20 × 0.20 mm) for the title complex was selected and mounted on a Bruker Smart 1000 diffractometer with graphite-monochromatized MoKα radiation ($\lambda = 0.71073$ Å), using the ω scan technique at 293(2) K. Some 3239 reflections were measured in the range $2.41° \leq \theta \leq 23.29°$, and 1766 [$R$(int) = 0.0168] unique reflections with $I > 2\sigma(I)$ were used in the succeeding refinement. LP corrections were applied to the data.

The structure was solved by direct methods using SHELXS-97 [9] and refinement on F^2 was performed using SHELXL-97 by full-matrix least-squares techniques with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms positions were located in calculated positions and isotropically refined. Further details of the structure analysis are given in Table I.

RESULTS AND DISCUSSION

The structure of the compound consists of a discrete meutral dinuclear unit. A view of the dinuclear complex with atom labelling scheme is shown in Fig. 1 and selected bondlengths and angles are listed in Table II. Final atomic coordinates for all non-hydrogen atoms and equivalent thermal parameters are listed in Table III.

The two halves of the dimeric molecule are related by a crystallographic centre of symmetry. Two azido bridges link two Cd(II) ions in end-on mode. Each cadmium ion is in an distorted octahedral environment of three facially coordinated nitrogen atoms of the macrocyclic amine L, one nitrogen of a monodentate N_3 ligand and two nitrogen of a $\mu_{1,1}$-N_3 bridging group. The four-membered $Cd_2(\mu_{1,1}\text{-}N_3)_2$ ring is

TABLE I Crystal data and structure refinement details for the complex

Empirical formula	$C_{12}H_{30}Cd_2N_{18}$
Formula weight	651.34
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	8.467(3)
b (Å)	14.359(5)
c (Å)	10.115(4)
$\beta°$	95.026(6)
Volume (Å^3)	1225.1(8)
Z	4
Calculated density (g/cm^3)	1.766
Absorption coefficient (mm^{-1})	1.775
F(000)	648
Limiting indices	$-9 \leq h \leq 9$, $-15 \leq k \leq 13$, $-10 \leq l \leq 11$
Reflections collected/unique	4127/1766 [R(int) = 0.0168]
Completeness to $\theta = 23.29$	99.7%
Max. and min. transmission	0.7179 and 0.6653
Data/restraints/parameters	1766/0/145
Goodness-of-fit on F^2	1.013
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0194$, $wR2 = 0.0426$
R indices (all data)	$R1 = 0.0253$, $wR2 = 0.0441$

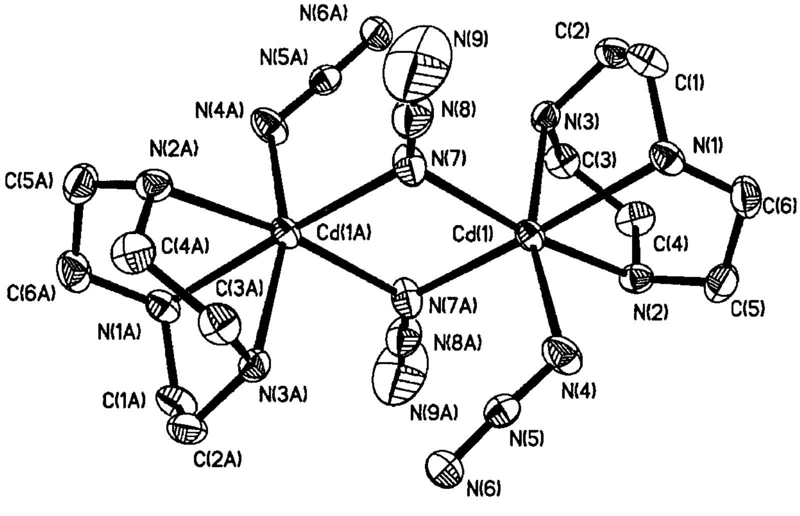

FIGURE 1 Perspective view of the complex $[L_2Cd_2(\mu\text{-}N_3)_2(N_3)_2]$ with the atom labelling scheme.

approximately planar, (∠N(1)–Cd(1)–N(1) = 78.66(10), ∠Cd(1A)–N(7)–Cd(1) = 101.34 (10)°) and the bridging azide group are linear, ∠N(7)–N(8)–N(9) being 179.2(4)°. One significant feature is the asymmetry of the bond distances between one azide bridge and two Cd(II) ions, Cd(1)–N(7) 2.346(3) and Cd(1A)–N(7) 2.329(2) Å. They are also asymmetric with the long N–N distances being between the central nitrogen atom and the nitrogen atom bonded to the Cd(II) ions. The Cd–N(macrocycle) distances, lying in the range 2.363(2)–2.376(2) Å, differ from those for other Cd–N(azide) distances, ranging between 2.304(2)–2.346(2) Å.

TABLE II Bondlengths (Å) and angles (°) for the complex

Cd(1)–N(4)	2.304(2)	Cd(1)–N(7)#1	2.329(2)
Cd(1)–N(7)	2.346(3)	Cd(1)–N(1)	2.363(2)
Cd(1)–N(2)	2.368(2)	Cd(1)–N(3)	2.376(2)
N(4)–N(5)	1.190(3)	N(5)–N(6)	1.165(3)
N(7)–N(8)	1.164(3)	N(7)–Cd(1)#1	2.329(2)
N(8)–N(9)	1.138(4)		
N(4)–Cd(1)–N(7)#1	97.79(9)	N(4)–Cd(1)–N(7)	95.40(10)
N(7)#1-Cd(1)–N(7)	78.66(10)	N(4)–Cd(1)–N(1)	88.93(8)
N(7)#1-Cd(1)–N(1)	172.45(8)	N(4)–Cd(1)–N(2)	95.86(9)
N(7)–Cd(1)–N(1)	104.23(9)	N(7)#1–Cd(1)–N(2)	100.41(8)
N(7)–Cd(1)–N(2)	168.73(9)	N(1)–Cd(1)–N(2)	75.37(9)
N(4)–Cd(1)–N(3)	162.38(8)	N(7)#1–Cd(1)–N(3)	98.58(9)
N(7)–Cd(1)–N(3)	94.17(9)	N(1)–Cd(1)–N(3)	74.37(8)
N(2)–Cd(1)–N(3)	74.79(8)	N(5)–N(4)–Cd(1)	122.93(19)
N(8)–N(7)–Cd(1)#1	129.9(2)	N(6)–N(5)–N(4)	177.4(3)
N(8)–N(7)–Cd(1)	127.8(2)	Cd(1)#1–N(7)–Cd(1)	101.34
N(9)–N(8)–N(7)	179.2(4)		

TABLE III Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for the complex

	x/a	y/b	z/c	U_{eq}
Cd(1)	6735(1)	489(1)	916(1)	35(1)
N(1)	9167(3)	86(2)	2102(2)	41(1)
N(2)	7439(3)	1816(2)	2225(2)	42(1)
N(3)	6098(3)	100(2)	3090(2)	39(1)
N(4)	8113(3)	913(2)	−855(2)	54(1)
N(5)	7509(3)	973(2)	−1959(3)	39(1)
N(6)	6967(3)	1051(2)	−3052(3)	53(1)
N(7)	5786(3)	−921(2)	−18(3)	49(1)
N(8)	6495(3)	−1603(2)	−161(3)	61(1)
N(9)	7204(5)	−2266(3)	−290(6)	154(2)
C(1)	8741(4)	−642(2)	3043(3)	52(1)
C(2)	7443(4)	−344(2)	3879(3)	49(1)
C(3)	5575(3)	997(2)	3617(3)	48(1)
C(4)	6787(4)	1759(2)	3536(3)	53(1)
C(5)	9175(4)	1824(2)	2273(3)	55(1)
C(6)	9939(4)	920(2)	2745(3)	58(1)

Structural data concerning the macrocyclic amine part of the complex are in agreement with a previous report dealing with compounds of the same ligand [10]. Due to the steric constraints of the macrocyclic ligand, the three respective N–Cd–N bond angles are smaller than 90° (average 74.84°). Cd–N distances of the coordinated amine are the same and longer than those of the azide ligands. Further, intermolecular hydrogen bonds are found between N–H groups of the macrocycle ligand and nitrogen atoms of the coordinated monodentate azides.

Acknowledgments

This work was supported by the Natural Science Foundation of China and the Teaching and Research Award Program for Outstanding Young Teachers in Higher Education Institutions of the Ministry of Education of China.

Supplementary Material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 192451. Copies of this information may be obtained free of charge from The Director, CCDC, 21 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www:gttp://www.ccdc.cam.ac.uk).

References

[1] (a) J.L. Manson, A.M. Arif and J.S. Miller, *Chem. Commun.* 1497 (1999); (b) E. Ruiz, J. Cano, S. Alvarez and P. Alemany, *J. Am. Chem. Soc.* **121**, 122 (1998); (c) J. Ribas, M. Monfort, X. Solans and M. Drillon, *Inorg. Chem.* **33**, 742 (1994); (d) A. Escuer, R. Vicente, M. Agoher and F.A. Mautner, *Inorg. Chem.* **36**, 440 (1997); (e) R. Cortes, L. Lezama, F.A. Mautner and T. Rojo, In: M.M. Turbull, T. Sugimoto and L.K. Thompson (Eds.), *Molecular Based Magnetic Materials* (American Chemical Society, Washington, 1996), pp. 193–195; (f) M.A.M. Abu-Youssef, M. Drillon, A. Escuer, M.A.S. Goher, F.A. Mautner and R. Vicente, *Inorg. Chem. Rev.* **193**, 195 (2000).

[2] (a) M.A. Aebersold, B. Gillon, O. Plantevin, L. Pardi, O. Kahn, P. Bergerat, I. Seggern, F. Tuczek, L. Ohrstrom, A. Grand and E. Lelievre-Berna, *J. Am. Chem. Soc.*, **120**, 5238 (1998); (b) M.H.W. Lam, Y.Y. Tang, K.M. Fung, X.X. You and W.T. Wong, *Chem. Commun.* 957 (1997); (c) A. Escuer, R. Vicente, M.S. El Fallah, M.A.S. Goger and F.A. Mautner, *Inorg. Chem.* **37**, 4467 (1998).

[3] T.C.W. Mak and M.A.S. Goher, *Inorg. Chim. Acta.* **115**, 15 (1986).

[4] F.A. Mautner and M.A.S. Goher, *Polyhedron*, **15**, 1133 (1996).

[5] M.I. Arriortua, A.R. Cortes, L. Lezam, T. Rojo, X. Solans and M. Font-Bardia, *Inorg. Chim. Acta* **174**, 263 (1990).

[6] R. Cortes, J.I. Ruiz de Larramendi, L. Lezama, T. Rojo, K. Urtiaga and M.I. Arriortua, *J. Chem. Soc., Dalton Trans.* 2723 (1992).

[7] A. Escuer, R. Vicente and J. Ribas, *J. Magn. Magn. Mater.* **110**, 181 (1992).

[8] (a) T.J. Atkins, J.E. Richman and W.F. Oettle, *Org. Synth.* **58**, 86 (1978); (b) K. Wieghardt, W. Schmidt and B. Nuber, *Ber.* 112 (1979).

[9] G.M. Sheldrick, *SHELXS-97 and SHELXL-97*, *Software for Crystal Structure Analysis* (Siemens Analytical X-ray Instruments Inc., Wisconsin, Madison, USA, 1997).

[10] G. Strasoleit, A.K. Duhme, M. Weber and S. Poh, *Acta Cryst.* **C48**, 437 (1992).