Synthesis and Crystal Structure of *cis*-Bis[1,3-bis(4-nitrophenyl)-triazenido $\kappa^2 N^1 N^3$]bis(pyridine- κN)cadmium(II), [Cd(O₂NC₆H₄NNNC₆H₄NO₂)₂(C₅H₅N)₂]

Manfredo HÖRNER,*† Deise Moreira BORCHARDT,* Jörg DANIELS,** and Johannes BECK**

*Departamento de Química, Universidade Federal de Santa Maria, Brazil

**Institut für Anorganische Chemie, Universität Bonn, Germany

The title complex was prepared by reaction of 1,3-bis(4-nitrophenyl)triazene with Cd(II) acetate in methanol/NaOH. Single crystals were obtained from pyridine and belong to the monoclinic space group *C2/c* with the lattice constants $a = 20.086(1)$, $b = 16.600(1)$, $c = 11.250(1)$ Å, $\beta = 102.122(1)^\circ$. The crystal structure consists of discrete mononuclear complexes of *C₂* symmetry, in which the Cd(II) ions have a distorted octahedral coordination environment. Two deprotonated 1,3-bis(4-nitrophenyl)triazene ions act as $N11-\eta^1$, $N13-\eta^1$ bidentate ligands. Two neutral pyridine molecules in the *cis* position complete the coordination sphere of the metal ion. The complexes are linked to chains *via* intermolecular non-classical C-H...O hydrogen bonds.

(Received April 24, 2006; Accepted September 25, 2006; Published on web December 28, 2006)

Besides the versatility of the coordination forms of triazene ligands, the coordination chemistry of this class of ligands has also attracted attention in connection with the analytical determination of heavy metal ions based on the chromogenic behavior of the respective complexes. 1,3-Diaryltriazene complexes, for example, were utilized for the spectrophotometric determination of cadmium(II).¹ To date, only two monocatenated diaryltriazene complexes of Cd(II) were characterized by single-crystal X-ray diffraction, namely [Cd(RNNNR)₂(C₅H₅N)₂] (R = *o*-FC₆H₄), in which the coordination geometry about the Cd(II) ion corresponds to a rhombically distorted octahedron, and K[Cd(O₂NC₆H₄NNNC₆H₄NO₂)₃], an anionic cadmium(II) complex in which the Cd atom is coordinated in a trigonal-prismatic arrangement by three 1,3-bis(4-nitrophenyl)triazene anions.^{2,3}

The synthesis of the title complex included reagents and solvents of reagent grade, which were used without further purification. 1,3-bis(4-nitrophenyl)triazene was prepared according to a previously reported method.⁴ Yellow 1,3-bis(4-nitrophenyl)triazene (47 mg, 0.16 mmol) was dissolved in methanol (20 mL) and treated with sodium hydroxide (197 mg, 3.51 mmol) resulting in an intense-red mixture. A solution of cadmium(II) acetate dihydrate (21.3 mg, 0.08 mmol) in methanol (10 mL) was added slowly with continuous stirring; the color of the reaction mixture changed to orange-red. After 2 h of stirring at room temperature, an orange-red microcrystalline precipitate was isolated and dried under vacuum. The precipitate was dissolved in 10 mL of pure pyridine. Orange-red block-shaped crystals of [Cd(O₂NC₆H₄NNNC₆H₄NO₂)₂(C₅H₅N)₂] suitable for X-ray diffraction were obtained by slow evaporation of the solvent at room temperature within two weeks. Yield, 38% (25.6 mg); m.p., 228°C (decomposition). IR (KBr pellet, cm⁻¹), 1225.0 (ν_{as} NNN) vs; 1504.7 (ν_{as} NO₂) s; 1328.4 (ν_s NO₂) s. (IR data: vs,

very strong; s, strong).

The X-ray data were collected by graphite-monochromated Mo K_α radiation ($\lambda = 0.71073$ Å). The crystal and experimental data are listed in Table 1. The structure was solved by direct

Table 1 Crystal and experimental data

Formula: C ₃₄ H ₂₆ CdN ₁₂ O ₈
Formula weight: 843.07
Crystal system: monoclinic
Space group: <i>C2/c</i> Z = 4
$a = 20.086(1)$ Å
$b = 16.600(1)$ Å
$c = 11.250(1)$ Å
$\beta = 102.122(1)^\circ$
$V = 3667.1(2)$ Å ³
$D_x = 1.527$ g/cm ³
Absorption coefficient = 0.663 mm ⁻¹
$F(0\ 0\ 0) = 1704$
Crystal dimensions (mm) = 0.32 × 0.25 × 0.20
Final <i>R</i> indices [$I > 2\sigma(I)$]: $R_1 = 0.0370$, $wR_2 = 0.0936$
<i>R</i> indices (all data): $R_1 = 0.0584$, $wR_2 = 0.1184$
θ range for data collection: 1.61 to 25.50°
Goodness-of-fit = 1.000
$(\Delta\rho)_{\max} = 0.301$ e.Å ⁻³
$(\Delta\rho)_{\min} = -0.564$ e.Å ⁻³
Reflections collected = 18159
Independent reflections = 3425 [$R_{\text{int}} = 0.0573$]
No. of reflections used = 3425
No. of parameters = 249
Data collection: Nonius KappaCCD area-detector diffractometer ⁷
Cell refinement: HKL SCALEPACK ⁸
Data reduction: HKL DENZO ⁸ and SCALEPACK
Molecular graphics: DIAMOND ⁹
Absorption correction: analytical ¹⁰

CCDC 293521 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

† To whom correspondence should be addressed.
E-mail: hoerner@smail.ufsm.br

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

Cd-N11	2.282(3)	N11-Cd-N11'	108.6(1)
Cd-N31	2.344(3)	N11-Cd-N31	88.9(1)
Cd-N13	2.499(3)	N11-Cd-N31'	151.4(1)
N1-C14	1.465(5)	N13-Cd-N13'	146.0(1)
N11-N12	1.298(4)	N31-Cd-N13	103.1(1)
N12-N13	1.311(4)	N31'-Cd-N13	101.8(1)
N13-C21	1.390(4)	N31'-Cd-N31	85.2(2)
		N11-Cd-N13	52.5(1)
		N11-Cd-N13'	105.5(1)
		N11-N12-N13	109.0(3)

Symmetry transformations used to generate equivalent atoms: (') 1 - x, y, 1/2 - z.

methods using SHELXS97.⁵ The non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method using SHELXL97.⁵ The positional parameters of the H atoms were obtained geometrically, with the C-H distances fixed (0.93 Å for Csp^2), and refined as riding on their respective C atoms, with $U_{iso}(H) = 1.2U_{eq}(Csp^2)$. Selected bond distances and angles are given in Table 2. A chemical diagram and the molecular structure of the title complex are shown in Figs. 1 and 2, respectively.

The crystal structure consists of discrete mononuclear complexes with site symmetry 2. The Cd(II) ion has a rhombically distorted octahedral coordination environment (Fig. 2). Two deprotonated 1,3-bis(4-nitrophenyl)triazene ions act as N11- η^1 , N13- η^1 bidentate (four-electron donor) ligands, and two neutral pyridine molecules in the *cis* position to each other complete the coordination sphere of the metal ion.

In the molecule, the Cd(II) ion is situated in a distorted square-planar base established by atoms N11, N11', N31, N31' [r.m.s. deviation = 0.5169 Å; symmetry code: (') 1 - x, y, 1/2 - z]. The crystallographic twofold-symmetry axis bisects the N31-Cd-N31' [85.2(2)°] and N11-Cd-N11' [108.6(1)°] angles, and the N13-Cd-N13' [146.0(1)°] axial angle. These values are in good agreement with those found in the Co(II) triazene complex $[Co(C_{12}H_{10}N_3)_2(C_5H_5N)_2]$, also with Co(II) on a crystallographic twofold-symmetry axis $[N4-Co-N4'' = 89.6(1)^\circ, N3-Co-N3'' = 90.3(1)^\circ$ and $N1-Co-N1'' = 149.6(1)^\circ$; symmetry code: (") -x, 1 - y, z].⁶ The Cd-N11 [2.282(3)Å], Cd-N13 [2.499(3)Å] and Cd-N31 [2.344(3)Å] bond distances are in good agreement with those found in $[Cd(RNNNR)_2(C_5H_5N)_2]$ (R = *o*-FC₆H₄) Cd-N11 [2.376(2)Å], Cd-N13 [2.380(2)Å] and Cd-N31 [2.346(2)Å].² Due to the bidentate coordination mode of the triazene ligand, together with the acute N11-Cd-N13 angle [52.5(1)°], the Cd/N11-N11-N13 four-membered chelate ring is strained. The bond angle of the N11-N12-N13 triazene chain [109.0(3)°] is close to that found in $[Cd(RNNNR)_2(C_5H_5N)_2]$ (R = *o*-FC₆H₄) [109.5(2)°].² The phenyl rings are planar within the experimental error [mean r.m.s. deviation 0.0057 Å] and make an interplanar angle of 10.6(2)°, indicating that the whole triazene ligand deviates slightly from planarity [r.m.s. deviation 0.1598 Å].

In the crystal structure, molecules related by an axial *n*-glide plane are linked into chains along the [101] direction *via* intermolecular non-classical C-H...O hydrogen bonds $[C33...O11' = 3.140(6)$ Å and $C33-H33...O11' = 120.33^\circ$; symmetry code: (") 1/2 - x, 1/2 - y, -z]; these chains are related in pairs through an inversion centre, without bidimensional interactions.

The pyridine ring exhibits a dihedral angle of 56.3(1)° with an axial N13-Cd-N13' moiety, and is close to that found in $[Cd(RNNNR)_2(C_5H_5N)_2]$ (R = *o*-FC₆H₄) [56.4(6)°].²

Fig. 1 Chemical diagram.

Fig. 2 Molecular structure of the Cd(II) complex with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. Symmetry code: (') 1 - x, y, 1/2 - z].

Acknowledgements

This work received partial support from CNPq (Proc. 475294/2004-1), and FAPERGS/PRONEX (Proc. 98/0451.6). MH thanks CNPq (Proc. 301310/2003-3) for grant. Diffractometer was supported by the Financiadora de Estudos e Projetos (FINEP, CT/Infra 03/2001).

References

1. Y. Hayashibe and Y. Sayama, *Analyst*, **1996**, 121, 7.
2. M. Hörner, V. S. Carratu, J. Bordinhão, A. Silva, and E. Niquet, *Acta Crystallogr.*, **2004**, C59, m140.
3. M. Hörner, V. S. Carratu, R. Herbst-Irmer, C. M. Mössmer, and J. Strähle, *Z. Anorg. Allg. Chem.*, **2003**, 629, 219.
4. M. Hörner, L. Bresolin, J. Bordinhão, E. Hartmann, and J. Strähle, *Acta Crystallogr.*, **2003**, C59, o426.
5. G. M. Sheldrick, *SHELXS97* and *SHELXL97*, **1997**, University of Göttingen, Germany.
6. S.-M. Peng, Y.-N. Lin, and Y. Wang, *Bull. Inst. Chem. Acad. Sin.*, **1985**, 32, 1.
7. Nonius *COLLECT*, **1997 - 2000**, Nonius BV, Delft, The Netherlands.
8. Z. Otwinowski and W. Minor, "Methods in Enzymology, Macromolecular Crystallography", Part A, ed. C. W. Carter Jr. and R. M. Sweet, New, York, Academic Press, **1997**, Vol. 276, 307.
9. K. Brandenburg, *DIAMOND*, **2004 - 2005**, Version 3.1. Crystal Impact GbR, Bonn, Germany.
10. N. W. Alcock, *Crystallographic Computing*, Ed. by F. R. Ahmed, S. R. Hall, and P. Huber, Copenhagen, Munksgaard, **1970**, 271.