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Synthesis, Characterization, and Crystal Structure of a Novel Acetato-bridged Trinuclear Cadmium(II) Complex with 4-Nitro-2-[(2-isopropylaminoethylimino)methyl]phenol

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A novel acetato-bridged centrosymmetric trinuclear Schiff base cadmium(II) complex, $[Cd\{CdL(\mu_2-O,O'\text{-}CH_3COO)(\mu_3-O,O,O'\text{-}CH_3COO)\}_2]$, where L is the deprotonated form of 4-nitro-2-[(2-isopropylaminoethylimino)methyl]phenol, has been synthesized and characterized by elemental analysis, IR spectrum, and single crystal X-ray diffraction. The acetate groups bridge adjacent Cd atoms through both μ_2-O,O'-acetato and μ_3-O,O,O'-acetato bridging modes. The Cd atoms adopt octahedral coordinations. The Cd···Cd distance is 3.434(2) Å.

Keywords acetate, cadmium complex, crystal structure, Schiff base, synthesis

INTRODUCTION

Schiff bases have been widely used as chelating ligands in the field of coordination chemistry for their versatile structures and potential applications.[1–3] The acetate anions can link two or more metal atoms through μ_2-acetato-O,[4,5] μ_2-acetato-O,O',[6,7] and μ_3-acetato-O,O,O'[7,8] bridging modes (Scheme 1), yielding various polynuclear and one-, two-, or three-dimensional species of different topologies. In the present work, a novel centrosymmetric trinuclear cadmium complex, $[Cd\{CdL(\mu_2-O,O'\text{-}CH_3COO)(\mu_3-O,O,O'\text{-}CH_3COO)\}_2]$, where L is the deprotonated form of 4-nitro-2-[(2-isopropylaminoethylimino)methyl]phenol (HL, Scheme 2), has been synthesized and structural characterized.

EXPERIMENTAL

Materials and Instrumentation

Infrared spectra were recorded in a Bruker IFS-125 model FT-IR spectrophotometer as KBr pellets. C, H, N analyses were carried out using a Perkin-Elmer model 240 analyzer. The ^{1}H NMR spectrum was recorded on Bruker AVANCE 500 MHz spectrometer with tetramethylsilane as the internal reference. 5-Nitrosalicylaldehyde and N-isopropylethane-1,2-diamine were purchased from Lancaster Company, and other chemicals were of analytical grade quality and used without further purification.

Synthesis of HL

To a methanol solution (10 ml) of 5-nitrosalicylaldehyde (1.0 mmol, 167 mg) was added a methanol solution (10 ml) of N-isopropylethane-1,2-diamine (1.0 mmol, 102 mg), with continuous stirring at room temperature. The mixture was stirred for about 10 minutes and most of the solvent was evaporated to give yellow solid, which was filtered out and dried in air. Yield: 233 mg (93%). M.p. 72.0–73.5°C. Analysis: calcd. for $C_{12}H_{17}N_3O_3$: C, 57.4; H, 6.8; N, 16.7%. Found: C, 57.1; H, 6.9; N, 17.0%. Selected IR data (KBr, cm^{-1}): 3422 (w, br), 3300 (m, sh), 3067 (w), 2956 (m), 2894 (w), 2833 (w), 1637 (vs), 1540 (s), 1523 (s), 1439 (s), 1376 (m), 1307 (vs), 1228 (s), 1171 (m), 1132 (m), 1093 (s), 1041 (w), 892 (w), 837 (w), 736 (w), 680 (w), 629 (w), 487 (w). ^{1}H NMR data (CDCl$_3$, ppm): $\delta = 1.05$ (d, 6H), 2.13 (s, 1H), 2.93 (t, 2H), 2.98 (m, 1H), 3.58 (t, 2H), 7.09 (d, 1H), 8.07 (d, 1H), 8.12 (s, 1H), 8.36 (s, 1H).

Synthesis of $[Cd\{CdL(\mu_2-O,O'\text{-}CH_3COO)(\mu_3-O,O,O'\text{-}CH_3COO)\}_2]$

To a methanol solution (30 ml) of HL (0.5 mmol, 125 mg) was added a methanol solution (10 ml) of $Cd(CH_3COO)_2\cdot 2H_2O$ (1.0 mmol, 266 mg), with continuous stirring at room temperature. The final clear solution was allowed to stand at room temperature for several days. Colorless crystals suitable for X-ray diffraction were collected and dried in air. Yield: 172 mg (64% with respect to the HL). M.p. > 300°C. Analysis: Calcd. for $C_{32}H_{44}Cd_3N_6O_{14}$: C, 35.8; H, 4.1; N, 7.8%. Found: C, 35.1; H, 4.3; N, 8.2%. Selected IR data (KBr, cm^{-1}): 3447 (w, br), 3213 (m, sh), 1648 (s), 1599 (s), 1402 (s), 1310 (s), 1105 (m).

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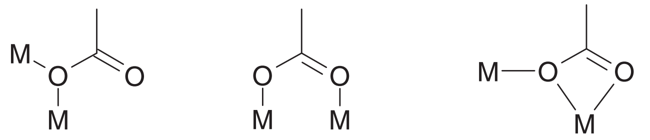
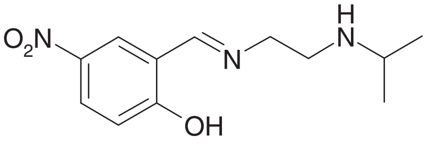


μ_2-acetato-*O* μ_2-acetato-*O,O'* μ_3-acetato-*O,O,O'*

SCH. 1. The bridging modes of the acetate groups.



SCH. 2. The Schiff base HL.

Crystal Structure Determination

A selected high quality crystal of the complex was mounted on a glass fiber and aligned on the Bruker SMART 1000 CCD diffractometer, equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The θ range for data collection is 2.09–27.50° for the complex. All data were corrected for Lorentz and polarization effects and for the effects of absorption. The structure was solved by the direct method and refined by least-square cycles. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C−H distances in the range 0.93−0.97 Å, N−H distances of 0.91 Å, and with U_{iso}(H) set at 1.2U_{eq}(C, N) and 1.5U_{eq}(methyl C). All calculations were performed using the SHELXTL-97 package.[9] The data collection and refinement parameters are summarized in Table 1. Selected bond lengths and angles are given in Table 2.

TABLE 1
Crystallographic and experimental data for the complex

Formula	$C_{32}H_{44}Cd_3N_6O_{14}$
FW	1073.9
Crystal shape / color	Block/colorless
Crystal size / mm	0.32 × 0.29 × 0.27
Crystal system	Triclinic
Space group	P-1
a/Å	10.2169(13)
b/Å	10.4570(13)
c/Å	11.1057(14)
α /°	114.444(1)
β /°	105.449(2)
γ /°	91.724(2)
V/Å^3	1027.7(2)
Z	1
T/K	298(2)
μ / mm^{-1}(Mo-Kα)	0.71073
D_{calc}/g cm^{-3}	1.735
Reflections/parameters	4550/254
Independent reflections	3808
R_{int}	0.0172
Restraints	0
F(000)	534
T_{min}	0.6275
T_{max}	0.6709
Goodness of fit on F^2	1.043
R_1, wR_2 [$I \geq 2\sigma(I)$]$^{a)}$	0.0264, 0.0702
R_1, wR_2 (all data)$^{a)}$	0.0323, 0.0724

$R_1 = \sum||F_o| - |F_c|| \,/\, \sum|F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$

RESULTS AND DISCUSSION

Synthesis

The Schiff base HL was readily synthesized by the condensation of equimolar quantities of 5-nitrosalicylaldehyde with N-isopropylethane-1,2-diamine in methanol, with high yield and purity. The cadmium complex was synthesized by reaction of HL with cadmium acetate in methanol (Scheme 3).

To our knowledge, only one copper(II) complex[10] and one zinc(II) complex[11] with the Schiff base ligand L were reported. Both complexes are mononuclear. We have tried to use the $CdCl_2$ and $Cd(NO_3)_2$ as the starting material in the preparation of the complex; however, it is difficult to obtain the single crystals.

X-ray Crystal Structure of the Complex

The molecular structure of the complex is shown in Figure 1. The complex is an acetato-bridged centrosymmetric trinuclear cadmium(II) complex, with the Cd1 atom lying on the inversion center. It is very interesting that the acetate ligands adopt two different bridging modes, *viz.* μ_2-acetato-O,O' and μ_3-acetato-O,O,O'.

The Cd1 atom is six-coordinated by two oxygen bridges, O1 and O1A, from two Schiff base ligands, and by four O atoms from four acetate bridges, forming an octahedral geometry. The coordination around the central metal atom displays only slight distortion. The bond distances are relatively similar and range from 2.212(2) to 2.320(2) Å. The greatest deviation of the bond angles from those expected for an ideal octahedral geometry is found for O1-Cd1-O6 with 79.0(1)°, which is caused by the strain created by the four-membered chelate ring Cd1-O1-Cd2-O6.

The coordination around the inversion-related terminal Cd2 atoms is also octahedral for the complex, but with severe distortion. The octahedron of each terminal Cd2 atom is formed by one phenolate O, one imine N and one amine N atoms of L, and by three O atoms from two acetate ligands. The distortion of the octahedral geometry is mainly caused by the strain created by the four-membered chelate rings Cd1-O1-Cd2-O6 and

TABLE 2
Selected bond lengths (Å) and angles (°) for the complex

Bond lengths			
Cd1-O1	2.320(2)	Cd1-O5	2.212(2)
Cd1-O6	2.299(2)	Cd2-O1	2.321(2)
Cd2-N1	2.263(2)	Cd2-N2	2.323(2)
Cd2-O4	2.231(2)	Cd2-O6	2.297(2)
Cd2-O7	2.497(2)		
Bond angles			
O5-Cd1-O5A	180	O5-Cd1-O6	87.0(1)
O5-Cd1-O6A	93.0(1)	O6-Cd1-O6A	180
O5-Cd1-O1A	91.5(1)	O6-Cd1-O1A	101.0(1)
O5-Cd1-O1	88.5(1)	O6-Cd1-O1	78.9(1)
O1-Cd1-O1A	180	O4-Cd2-N1	114.4(1)
O4-Cd2-O6	90.4(1)	N1-Cd2-O6	147.5(1)
O4-Cd2-O1	93.4(1)	N1-Cd2-O1	78.9(1)
O6-Cd2-O1	79.0(1)	O4-Cd2-N2	92.9(1)
N1-Cd2-N2	76.6(1)	O6-Cd2-N2	125.0(1)
O1-Cd2-N2	155.2(1)	O4-Cd2-O7	138.3(1)
N1-Cd2-O7	107.1(1)	O6-Cd2-O7	53.8(1)
O1-Cd2-O7	98.8(1)	N2-Cd2-O7	92.4(1)

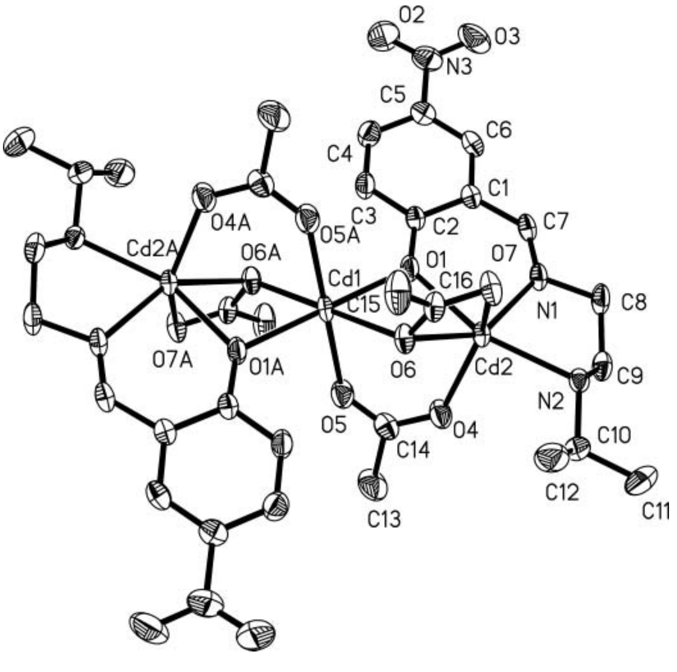


FIG. 1. Molecular structure of the complex with 30% probability displacement. H atoms are omitted for clarity.

Cd2-O6-C16-O7, and the five-membered chelate ring Cd2-N1-C8-C9-N2.

The coordinate bond lengths in the complex are comparable to the similar Schiff base cadmium(II) complexes.[12–14] The Cd···Cd distance is 3.434(2) Å, which precludes any significant metal-metal interaction.

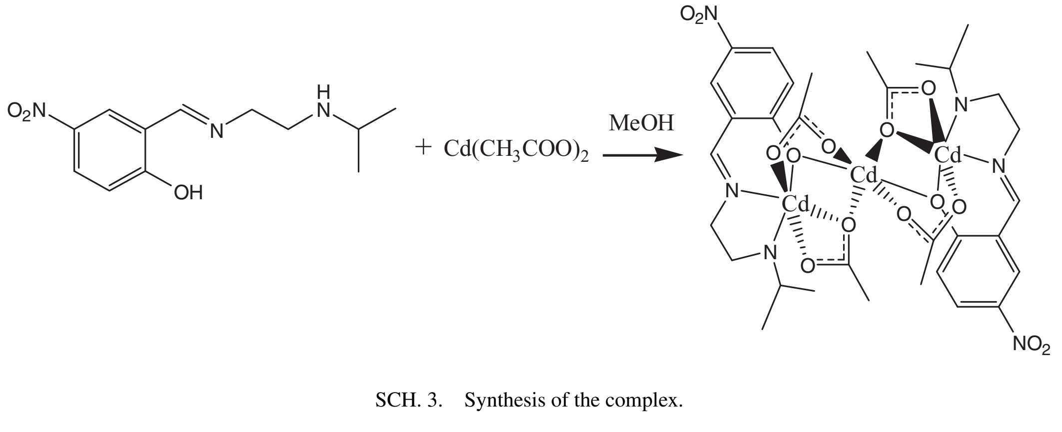
In the crystal structure of the complex, molecules are linked through intermolecular N—H···O hydrogen bonds, forming chains running along the *c* axis, as shown in Figure 2.

SUMMARY

In the above study, a novel acetato-bridged centrosymmetric trinuclear cadmium(II) complex with the Schiff base 4-nitro-2-[(2-isopropylaminoethylimino)methyl]phenol was synthesized and characterized. The crystal structure of the complex was investigated. The Schiff base coordinates to the Cd atom through the phenolate O, imine N and amine N atoms. The acetate anions adopt two different bridging modes, *viz.* μ_2-acetato-O,O' and μ_3-acetato-O,O,O'.

SUPPLEMENTARY MATERIAL

Crystallographic data for the complex has been deposited with the Cambridge Crystallographic Data Centre, CCDC reference number 638094. Copies of these information may be obtained free of charge from: the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).



SCH. 3. Synthesis of the complex.

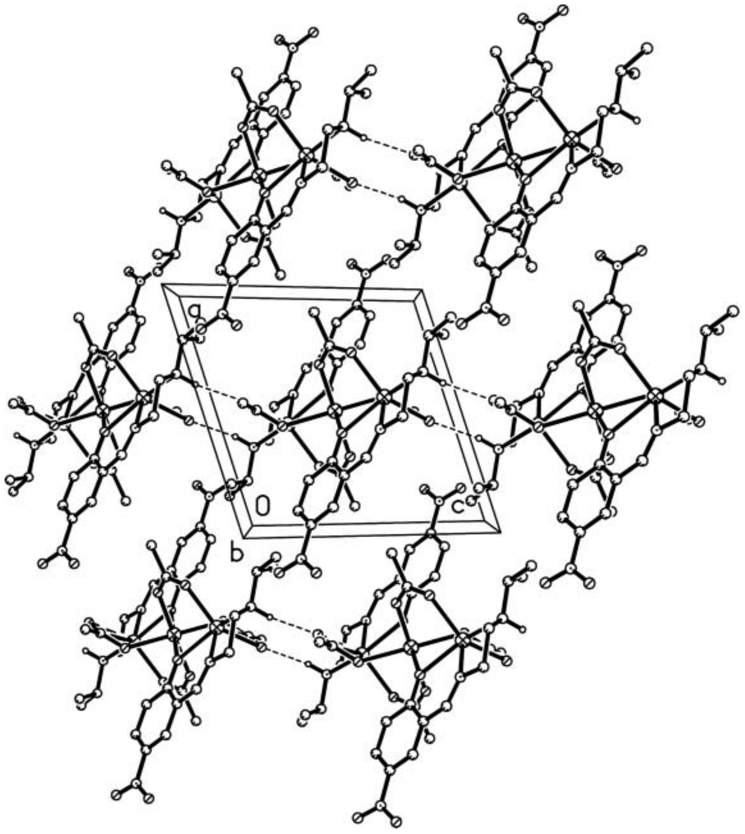


FIG. 2. Molecular packing of the complex, viewed along the *b* axis. Hydrogen bonds are shown as dashed lines.

REFERENCES

1. Yue, Y.-F., Gao, E.-Q., Fang, C.-J., Zheng, T., Liang, J., and Yan, C.-H. The crystal structures of four azido-bridged Zn(II) complexes based on open-chain diazine Schiff-base ligands. *Cryst. Eng. Comm.*, **2008**, 10, 614–622.
2. Pessoa, J.C., Correia, I., Galvão, A., Gameiro, A., Felix, V., and Fiuza, E. Enantioselectivity in Ni(II) Schiff-base complexes derived from amino acids and (*S*-)*o* − *N*-(*N*-benzylprolyl)aminobenzophenone. Molecular structure of several chiral Ni(II) Schiff-base complexes, circular dichroism and molecular mechanics studies. *Dalton Trans.*, **2005**, 2312–2321.
3. Black, D., Blake, A.J., Finn, R.L., Lindoy, L.F., Nezhadali, A., Rougnaghi, G., Tasker, P.A., and Schröder, M. Compartmental Schiff-base ligands as selective double-loaded extractants for copper(II). *Chem. Commun.*, **2002**, 340–341.
4. Hämäläinen, R., Ahlgrén, M., and Turpeinen, U. Structure of acetato(*N*-methyl-*N*′-salicylidene-1,3-propanediaminato)copper(II) dimer. *Acta Crystallogr.*, **1982**, *B*38, 1577–1580.
5. Demšar, A., Košmrlj, J., and Petriek, S. Variable-temperature nuclear magnetic resonance spectroscopy allows direct observation of carboxylate shift in zinc carboxylate complexes. *J. Am. Chem. Soc.*, **2002**, 124, 3951–3958.
6. Adams, H., Fenton, D.E., McHugh, P.E., and Potter, T.J. Dinuclear nickel(II) complexes of unsymmetric compartmental ligands bearing a terdentate linear arm and a terdentate dipodal arm. *Inorg. Chim. Acta.*, **2002**, 331, 117–122.
7. Picart, J.P., Sanchez, F.J., Casabó, J., Rius, J., Alvarez-Larena, A., and Ros, J. Synthesis and structural characterisation of a new cobalt(II) pentanuclear complex with a tetranucleating pyrazole-derived ligand. *Inorg. Chem. Commun.*, **2002**, 5, 130–133.
8. Koval, I.A., Gamez, P., Roubeau, O., Driessen, W.L., Lutz, M., Spek, A.L., and Reedijk, J. Century-known copper salt Cu(OAc)(OMe) proven to be a unique magnetic lattice composed of tetranuclear copper(II) species with a rare binding mode of the acetate anion. *Inorg. Chem.*, **2003**, 42, 868–872.
9. Sheldrick, G.M. *SHELXTL-97*, University of Göttingen: Germany, 1997.
10. Wang, C.-Y. Bis{2-[2-(isopropylamino)ethyliminomethyl]-4-nitro phenolato} copper(II) dinitrate. *Acta Crystallogr.*, **2007**, E63, m489–m491.
11. Wang, S.-X. Dichloro{2-[(2-isopropylaminoethylimino)methyl]-4-nitrophenolato}zinc(II). *Acta Crystallogr.*, **2007**, E63, m706–m707.
12. Atakol, O., Aksu, M., Ercan, F., Arici, C., Tahir, M.N., and Ülkü, D. A linear trinuclear Cd^{II}-Cd^{II}-Cd^{II} complex with a μ-acetato bridge: bis(μ-acetato)[-bis(salicylidene)-1,3-propanediaminato]cadmium(II)cadmium(II). *Acta Crystallogr.*, **1999**, C55, 1072–1075.
13. You, Z.-L., Zhu, H.-L., and Liu, W.-S. Solvolthermal syntheses and crystal structures of three linear trinuclear Schiff base complexes of zinc(II) and cadmium(II). *Z. Anorg. Allg. Chem.*, **2004**, 630, 1617–1622.
14. Lo, W.-K., Wong, W.-K., Wong, W.-Y., and Guo, J. Synthesis, crystal structures and photophysical properties of novel tetranuclear cadmium(II) Schiff-base complexes. *Eur. J. Inorg. Chem.*, **2005**, 3950–3954.