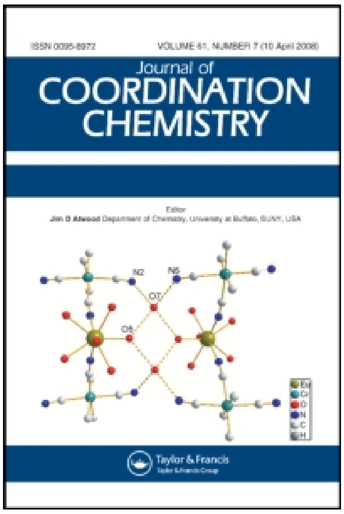

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Two new dinuclear complexes with flexible bipyrazole ligand bridged via μ-Cl or $\mu_{1,1}$-N_3

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Two new dinuclear complexes with flexible bipyrazole ligand bridged via μ-Cl or $\mu_{1,1}$-N$_3$

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Two dinuclear complexes, $\{[Cd(bdpp)Cl_2](CH_3OH)\}_2$ (**1**) and $[Cd(bdpp)(N_3)(NO_3)]_2$ (**2**), have been synthesized by reactions of bdpp with cadmium salts (bdpp = 1,3-*bis*(3′,5′-dimethylpyrazol-1′-yl)propane), and characterized by IR, element analysis, fluorescence properties and single crystal structural analysis. Cd in **1** has a trigonal bipyramidal coordination geometry and two such units form a dimer through two μ-Cl bridges. Each Cd in **2** has a distorted octahedral coordination geometry and two Cd units form a dimer through $\mu_{1,1}$-N$_3$ bridges. The emission spectra show $\lambda_{em} = 413$ nm for **1** and $\lambda_{em} = 338$ nm for **2**.

Keywords: Dinuclear complex; Bipyrazole ligand; Bridging ligand; Emission spectra

1. Introduction

Combined polypyrazole ligands, such as tris(3,5-dimethylpyrazolyl)methane, anionic tris(3,5-dimethylpyrazolyl)borate and their derivatives, have been studied extensively due to applications in magnetism [1], biological activity [2, 3] and catalysis [4, 5]. Flexible bipyrazole ligands as bidentate or bridging ligands have been less investigated. These ligands containing pyrazole groups separated by flexible three-carbon spacers, such as 1,3-*bis*(pyrazol-1′-yl)propane (bpp), 1,3-*bis*(5′-methylpyrazol-1′-yl)propane (bmpp) and 1,3-*bis*(3′,5′-dimethylpyrazol-1′-yl)propane (bdpp), have recently been reported [6–8]. The ligand bpp was reported as a bridging ligand to form a dinuclear silver complex [8]. Usually such ligands are bidentate, coordinating to one metal ion to form mononuclear complexes. For example, bpp or bdpp reacted with $ZnCl_2 \cdot H_2O$ in methanol to give mononuclear $[Zn(bpp)Cl_2]$ or $[Zn(bdpp)Cl_2]$ [7], but when $CdCl_2 \cdot 2.5H_2O$ instead of $ZnCl_2 \cdot H_2O$ was used a dinuclear complex $\{[Cd(bdpp)Cl_2](CH_3OH)\}_2$ (**1**), with μ-Cl bridge was formed. Differences for Zn and Cd chlorides have been observed [9, 10] with 2,2-bipyridine or 1,10-phenanthroline as ligands. The chloride as bridging ligand is common for Cd chlorides, but often a terminal for Zn chlorides. Similarly, bdpp with $Cd(NO_3)_2 \cdot H_2O$ and NaN_3 gave another

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dinuclear complex $[Cd(bdpp)(N_3)(NO_3)]_2$ (**2**). Complex **2** also is a dimer, linked by two $\mu_{1,1}$-N_3 bridges. The bdpp is bidentate instead of bridging in both complexes. In this article, we report the synthesis, structures and fluorescence properties of $\{[Cd(bdpp)Cl_2](CH_3OH)\}_2$ (**1**) and $[Cd(bdpp)(N_3)(NO_3)]_2$ (**2**).

2. Experimental section

2.1. *Materials and measurements*

All chemicals were reagent grade and used as received except bdpp, which was prepared according to the literature [7]. Elemental analyses were performed with a Vario ELIII CHNOS Element Analyzer. IR spectra were measured as KBr pellets on a Nicolet Magna 750 FT-IR spectrometer in the range of 400–4000 cm^{-1}. The fluorescence data were recorded on an Edinburgh FL-FS920 TCSPC system.

2.2. *Synthesis of the complexes*

2.2.1. $\{[Cd(bdpp)Cl_2](CH_3OH)\}_2$ (1). Complex **1** was obtained by dissolving 1.0 mmol (0.234 g) bdpp and 1.0 mmol (0.228 g) $CdCl_2 \cdot 2.5H_2O$ in 25 mL methanol and stirring for 6 h at room temperature. After slow evaporation for one week, block colorless crystals of **1** were isolated. Anal. Calcd for $C_{28}H_{48}Cd_2Cl_4N_8O_2$: C, 37.55; H, 5.36; N, 12.52, found: C, 37.42, H, 5.16; N, 12.47. Yields: 0.24 g (54%, based on Cd). IR (KBr, cm^{-1}): 3120 m, 2925 s, 2830 w, 1552 s, 1466 m, 1421 m, 1390 m, 1344 m, 1324 m, 1307 m, 1206 m, 1125 m, 1047 s, 1031 s, 977 m, 827 s, 798 s, 756 s.

2.2.2. $[Cd(bdpp)(N_3)(NO_3)]_2$ (2). Complex **2** was obtained by refluxing a solution of 1.0 mmol (0.234 g) bdpp and 1.0 mmol (0.308 g) $Cd(NO_3)_2 \cdot 4H_2O$ in 30 mL methanol for 10 min, then a solution of 0.10 g (1.51 mmol) NaN_3 in 10 mL methanol was added. After refluxing for 3.5 h, the crystal solid was collected by filtrating. The crystals suitable for diffraction were obtained from the cooled filtrate. Yields: 0.40 g (89%, base on Cd) Anal. Calcd for $C_{26}H_{40}Cd_2N1_6O_6$: C, 34.76; H, 4.46; N, 24.96. Found: C, 34.65; H, 4.28; N, 24.56. IR (KBr, cm^{-1}): 3379 m, 2964 w, 2306 w, 2146 m, 2063 s, 2050 s, 1618 w, 1556 s, 1497 m, 1438 s, 1384 m, 1340 m, 1287 s, 1206 m, 1123 m, 1043 s, 1030 s, 971 m, 809 s, 757 m, 661 s, 625 s.

2.2.3. X-ray crystallographic studies. The crystal structures of two complexes were studied by single-crystal X-ray diffraction. Data collection for **1** was performed at 130(2) K on a Rigaku Mercury CCD diffractometer and for **2** at 293(2) K on a Siemens SMART CCD diffractometer with graphite monochromatic Mo-Kα radiation ($\lambda = 0.71073$ Å). An empirical absorption correction was applied using the SADABS program [11]. The structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 by using the SHELX-97 program package [12]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of bdpp were generated geometrically. The crystallographic details for structure determinations of **1** and **2** are

Table 1. Crystallographic data collection and structure refinement.

Complex	**1**	**2**
Measurement device type	Mercury70 (2 × 2 bin mode)	Siemens SMART CCD
Empirical formula	$C_{28}H_{48}Cd_2C_24N_8O_2$	$C_{26}H_{40}Cd_2N_{16}O_6$
Fw	895.34	897.54
Temperature (K)	130(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $C2/c$
a (Å)	8.8695(1)	16.0834(2)
b (Å)	9.647(1)	15.4060(4)
c (Å)	12.0343(1)	14.9284(3)
α (°)	78.794(7)	90
β (°)	72.712(7)	106.0420(10)
γ (°)	66.099(6)	90
V (Å^3)	895.626(52)	3554.93(12)
Z	2	8
D_{Calcd} (mg m^{-3})	1.660	1.677
Absolute coefficient (mm^{-1})	1.524	1.259
F(000)	452	1808
Crytal size (mm^3)	0.75 × 0.35 × 0.18	0.34 × 0.28 × 0.22
θ range for data collection (°)	3.04–27.48	1.87–25.05
Limiting indices	$-11 \le h \le 11$, $-12 \le k \le 12$, $-15 \le l \le 13$	$-19 \le h \le 9$, $-13 \le k \le 18$, $-16 \le l \le 17$
Reflections collected/unique	6732/3982 [$R_{(int)} = 0.0131$]	5873/3102 [$R_{(int)} = 0.0267$]
Absorption correction	Multi-scan	Empirical
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3982/0/199	3102/0/227
Goodness-of-fit on F^2	1.050	1.035
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0276$, $wR_2 = 0.0779$	$R_1 = 0.0528$, $wR_2 = 0.1597$
R indices (all data)	$R_1 = 0.0291$, $wR_2 = 0.0787$	$R_1 = 0.0644$, $wR_2 = 0.1757$
Largest difference peak and hole (e Å^{-3})	0.686 and −1.015	0.673 and −0.728

$R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $R_w = \{\Sigma w[(F_o^2 - F_c^2)^2]/\Sigma w[(F_o^2)^2]\}^{0.5}$.

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Cd–N(4)	2.258(2)	N(4)–Cd–N(1)	106.80(7)	N(4)–Cd–Cl(1)#1	89.12(5)
Cd–N(1)	2.260(2)	N(4)–Cd–Cl(1)	124.23(5)	N(1)–Cd–Cl(1)#1	83.60(5)
Cd–Cl(1)	2.4733(6)	N(1)–Cd–Cl(1)	126.21(6)	Cl(1)–Cd–Cl(1)#1	81.52(2)
Cd–Cl(2)	2.5471(6)	N(4)–Cd–Cl(2)	94.52(5)	Cl(2)–Cd–Cl(1)#1	176.252(19)
Cd–Cl(1)#1	2.8415(6)	N(1)–Cd–Cl(2)	94.47(5)	Cd–Cl(1)–Cd#1	98.48(2)
Cl(1)–Cd#1	2.8415(6)	Cl(1)–Cd–Cl(2)	97.13(2)		

Symmetry transformations used to generate equivalent atoms: #1: $-x+2$, $-y+2$, $-z$.

listed in table 1. Selected bond distances and bond angles are given in tables 2 and 3, respectively.

3. Results and discussion

3.1. *Crystal structure of* $\{[Cd(bdpp)Cl_2](CH_3OH)\}_2$ *(1)*

The structure of the dinuclear complex is depicted in figure 1. Complex **1** has a symmetry center located between two cadmium ions. The ligand bdpp acts as a

Table 3. Selected bond lengths (Å) and angles (°) for **2**.

Cd–N(4)	2.305(6)	N(4)–Cd–N(1)	102.7(2)	N(5)–Cd–O(2)	93.3(2)
Cd–N(1)	2.310(6)	N(4)–Cd–N(5)	149.3(2)	N(5)#1–Cd–O(2)	167.0(2)
Cd–N(5)	2.317(6)	N(1)–Cd–N(5)	107.6(2)	N(4)–Cd–O(1)	81.6(2)
Cd–N(5)#1	2.331(6)	N(4)–Cd–N(5)#1	97.9(2)	N(1)–Cd–O(1)	36.2(2)
Cd–O(2)	2.363(6)	N(1)–Cd–N(5)#1	98.0(2)	N(5)–Cd–O(1)	79.8(2)
Cd–O(1)	2.580(8)	N(5)–Cd–N(5)#1	73.7(3)	N(5)#1–Cd–O(1)	125.0(2)
N(6)–N(5)	1.143(9)	N(4)–Cd–O(2)	93.4(2)	O(2)–Cd–O(1)	50.5(2)
N(6)–N(7)	1.177(10)	N(1)–Cd–O(2)	85.7(2)	Cd–N(5)–Cd#1	106.3(3)

Symmetry transformations used to generate equivalent atoms: #1: $-x+1/2$, $-y+1/2$, $-z$.

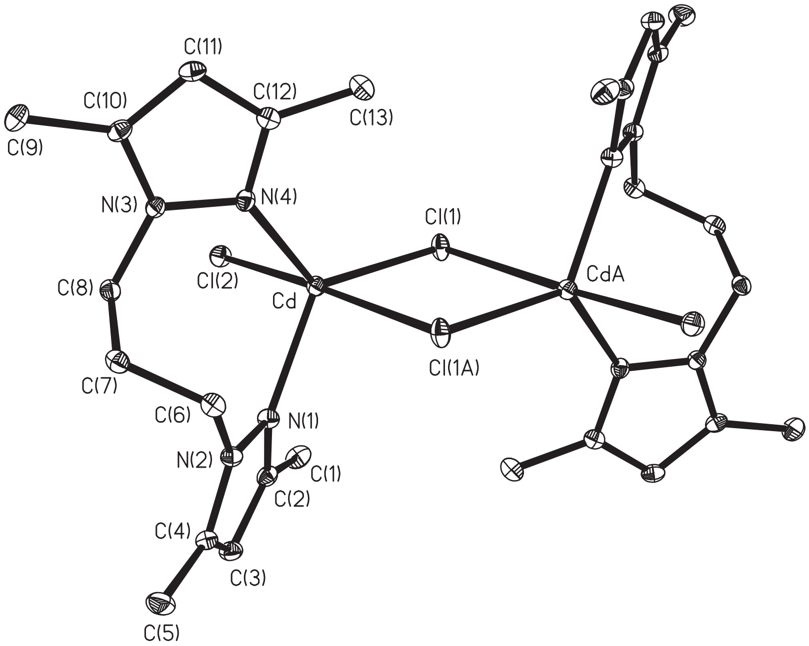

Figure 1. Molecular structure of **1**, the methanol molecules are omitted for clarity.

bidentate ligand with N(1) and N(4) as coordinating atoms. The coordination geometry around Cd can best be described as a distorted trigonal bipyramid with the trigonal plane generated by N(1), N(4) and Cl(1) atoms (N(4)–Cd–N(1) 106.80(7)°, N(4)–Cd–Cl(1) 124.23(5)°, N(1)–Cd–Cl(1) 126.21(6)°), and the Cl(2) and Cl(1a) atoms located at apical positions. The Cd is coordinated with two nitrogen atoms from bdpp (Cd–N(1) 2.260(2) Å, Cd–N(4) 2.258(2) Å) and three chloride atoms (Cl(1), Cl(1a) and Cl(2)). Cl(1) and Cl(1a) are bridging ligands to form a dimer (Cd–Cl(1) 2.4733(6) Å, Cd–Cl(1a) 2.8415(6) Å), and Cl(2) atom is terminal (Cd–Cl(2) 2.5471(6) Å). The Cd deviates slightly (−0.1670 Å) from the least-square plane (N(1), N(4), Cl(1), Cd). The angle Cl(2)–Cd–Cl(1a), formed by two apical Cl atoms of the trigonal bipyramidal with Cd atom, is 176.252(19)°. There are two methanol molecules in **1**, which play an important role in forming and stabling the compound. When solvent molecules were lost, the colorless crystals of **1** decomposed.

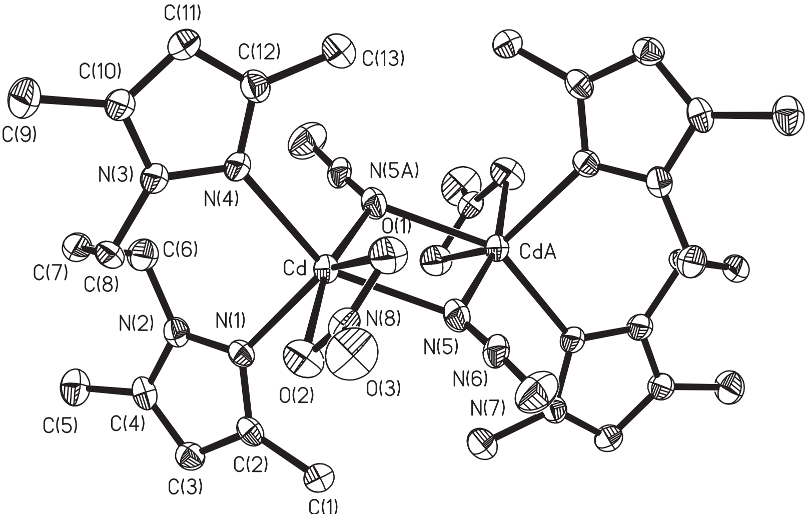

Figure 2. Molecular structure of **2**.

3.2. *Crystal structure of* $[Cd(bdpp)(N_3)(NO_3)]_2$ *(2)*

The structure of dinuclear **2** is depicted in figure 2. Unlike **1**, in **2**, the cadmium is distorted octahedral. This complex consists of a centrosymmetric pair of cadmium ions bridged by two μ-(1,1)-azido anions. The ligand bdpp also is bidentate as in **1**. The Cd atom is coordinated with one bdpp ligand, two azide ions (Cd–N(1) 2.310(6) Å, Cd–N(4) 2.305(6) Å, Cd–N(5) 2.317(6) Å, Cd–N(5a) 2.331(6) Å) and two oxygen atoms from one nitrate ion (Cd–N(1) 2.310(6), Cd–N(4) 2.305(6) Å). The bond lengths of Cd–N and Cd–O are comparable with those previously reported [13–16]. The Cd–N(5) and Cd–N(5a) distances are slightly different (0.014 Å), indicating the azido group has been delocalized, also supported by the bond lengths of azide (N(6)–N(5) 1.143(9), N(6)–N(7) 1.177(10) Å). The N(1)–Cd–N(4) angle is 102.7(2)°, reduced by 4.1° from the corresponding angle of **1**. The angles of N(5)–Cd–N(5A) and Cd–N(5)–CdA are 73.7(2) and 106.3(3)°, respectively.

3.3. *Spectra properties*

The IR spectrum of **2** shows two sharp peaks at $2050\,\mathrm{cm}^{-1}$ and $2063\,\mathrm{cm}^{-1}$, falling in the range for azide bridging modes summarized by Rojo *et al.* [17]. These two bonds can be assigned to μ-(1,1)-azide coordination although absorption at $2060\,\mathrm{cm}^{-1}$ has been ascribed to a mixed mode for azide by some reports [18, 19]. Our assignment is in accord with the crystal structure of **2**.

Intense emission bands are observed at 413 nm ($\lambda_{ex} = 304$ nm) for **1** and 338 nm ($\lambda_{ex} = 302$ nm) for **2**, respectively, assigned to ligand-to-metal charge-transfer (LMCT) transitions. For **2**, the emission band is adjacent to the excitation band, probably resulting from the two delocalized μ-(1,1)-azide groups making the structure more rigid and promoting couplings between metal atoms [20].

4. Conclusion

We have synthesized two dinuclear complexes with bdpp ligands. These complexes illustrate that flexible bipyrazole ligands with some metal salts offer the possibility of new multinuclear complexes when a bridging ligand is introduced. The fluorescence properties also show these complexes have potential applications as emission materials.

Supplementary material

Crystallographic data for complexes **1** and **2** have been deposited with Cambridge Crystallographic Data Center, CCDC No. 602234 and 602235. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336-033; Email: deposit@ccdc.cam.ac.uk].

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References

[1] A.L. Thompson, A.E. Goeta, J.A. Real, A. Galet, M.C. Muñoz. *Chem. Commun.*, 1390 (2004).
[2] C. Bergquist, T. Fillebeen, M.M. Morlok, G. Parkin. *J. Am. Chem. Soc.*, **125**, 6189 (2003).
[3] M.P.K. Fujisawa, E.L. Hegg Jr. *J. Am. Chem. Soc.*, **125**, 7828 (2003).
[4] C. Tejel, J.M. Villoro, M.A. Ciriano, J.A. López, E. Eguizàbal, F.J. Lahoz, V.I. Bakhmutov, L.A. Oro. *Organometallics*, **15**, 2967 (1996).
[5] M.A. Esteruelas, M.P. García, A.M. López, L.A. Oro. *Organometallics*, **10**, 127 (1991).
[6] K. Flinzner, A.F. Stassen, A.M. Mills, A.L. Spek, J.G. Haasnoot, J. Reedijk. *Eur. J. Inorg. Chem.*, 671 (2003).
[7] A.M. Schuitema, M. Engelen, I.A. Koval, S. Gorter, W.L. Driessen, J. Reedijk. *Inorg. Chim. Acta*, **324**, 57 (2001).
[8] D.A. McMorran, S. Pfadenhauer, P.J. Steel. *Aust. J. Chem.*, **55**, 519 (2002).
[9] (a) D. Pucci, G. Barberio, A. Crispini, O. Francescangeli, M. Ghedini, M.L. Deda. *Eur. J. Inorg. Chem.*, 3649 (2003); (b) J.-D. Dalbavie, J.-B. Regnouf-de-Vains, R. Lamartine, M. Perrin, S. Lecocq, B. Fenet. *Eur. J. Inorg. Chem.*, 901 (2002); (c) H.-L. Kwong, K.-M. Lau, W.-S. Lee, W.-T. Wong. *New. J. Chem.*, **23**, 629 (1999).
[10] (a) D. Sun, R. Cao, Y. Liang, Q. Shi, W. Su, M. Hong. *J. Chem. Soc., Dalton Trans.*, 2335 (2001). (b) C. Janiak, S. Debon, H.-P. Wu, M.J. Kolm, P. Klufers, H. Piotrowski, P. Mayer. *Eur. J. Inorg. Chem.*, 1507 (1999).
[11] G.M. Sheldrick. *SADABS, Absorption Correction Program*, University of Göttingen, Germany (1996).
[12] G.M. Sheldrick. *SHELXS-97, Program for the Solution of Crystal Structures*, University of Göttingen, Germany (1997).
[13] E.A.H. Briffith, N.G. Charles, K. Lewinski, E.L. Amma, P.F. Rodesiler. *Inorg. Chem.*, **26**, 3983 (1983).
[14] R.-G. Xiong, X. Xue, H. Zhao, X.-Z. You, B.F. Abrahams, Z. Xue. *Angew. Chem., Int. Ed. Engl.*, **41**, 3800 (2002).
[15] M. Modal, M.K. Saha, S. Mitra, V. Gramlich. *Dalton Trans.*, 3218 (2000).

[16] M.-Y. Chow, X.-M. Chen, T.C.W. Mak. *J. Chem. Soc., Dalton Trans.*, 3413 (1993).
[17] R. Cortés, M. Drillon, X. Solans, L. Lezama, T. Rojo. *Inorg. Chem.*, **36**, 677 (1997).
[18] H.-J. Chen, X.-M. Chen. *Inorg. Chem. Acta*, **329**, 13 (2002).
[19] M.G. Barandika, R. Cortés, L. Lezama, M.K. Urtiaga, M.I. Arriortua, T. Rojo. *J. Chem. Soc., Dalton Trans.*, 2971 (1999).
[20] L. Han, M. Hong, R. Wang, J. Luo, Z. Lin, D. Yuan. *Chem. Commun.*, 2580 (2003).