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Cadmium(II) complexes containing *N*′-substituted *N*,*N*-bispyrazolyl ligands: The formation of 4- and 5-coordinated monomers versus 6-coordinated dimer



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ABSTRACT

Novel Cd(II) bromide complexes [L_aCdBr₂], [L_bCdBr₂] and [L_cCd(μ -Br)Br]₂ have been synthesized and characterized. [L_aCdBr₂] and [L_bCdBr₂] were distorted tetrahedral and trigonal bipyramidal geometry around metal, respectively, depending on the coordination of the nitrogen atom of N'-substituted amine moiety and the cadmium center. However, [L_cCd(μ -Br)Br]₂ reveals a bromo-bridged 6-coordinated dimeric species. Specifically, the catalytic activity of [L_bCdBr₂] (1.13 × 10⁵ g PMMA/mol Cd·h) in the polymerization of methyl methacrylate (MMA) in the presence of modified methylaluminoxane (MMAO) at 60 °C was higher than that of [L_aCdBr₂] (5.03 × 10⁴ g PMMA/mol Cd·h) and reference complex [CdCl₂] (3.53 × 10⁴ g PMMA/mol Cd·h).

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Transition metal complexes with pyrazole-based ligands have attracted attention because of their efficient synthesis and modification on a linker unit of two or three pyrazols [1-10]. Thus, pyrazolecontaining ligands can be designed to be coordinated to metals through monodentate, bidentate, tridentate, and tetradentate binding modes with various modifications of the ligand structure [11–19]. Accordingly, their structural properties often meet specific stereo-chemical requirements for specific metal-binding sites during catalysis. Specifically N,Nbidentate pyrazolyl-based chelating ligands were first reported by Driessen [20], these complexes show structural stability and catalytic ability, and have been applied to the areas of synthesis, structural design, and spectroscopy [3,8,9,12,14,16] and used for electronic materials, supra-molecules for metal-organic frame (MOF) applications [2,11], as catalysts for organic transformation [1,4,5,7], for biological applications [6,10,13], and for olefin polymerization [17-19]. Some recent studies have documented the use of transition metals, specifically cadmium [21–23], as a catalyst of methyl methacrylate (MMA) polymerization.

The Cd(II) bromide complexes [L_aCdBr_2], [L_bCdBr_2] and [$L_cCd(\mu$ -Br) Br]₂ were obtained from metal starting material [CdBr₂·4H₂O] with the corresponding ligands [L_n] (L_1 - L_3) in anhydrous ethanol with yields of 72%–85% (Scheme 1) [8,10,24].

The molecular structures of **[L_aCdBr₂]**, **[L_bCdBr₂]**, and **[L_cCd(μ-Br) Br**₂ are provided, and the selected bond distances and angles are listed in the captions of Figs. 1, 2, and 3, respectively.

The average Cd – N_{pyrazole} bond lengths ranged from 2.217(6) Å to 2.382(8) Å for Cd(II) complexes. The bond distance of Cd – N_{amine} in [LaCdBr2] was 3.687 Å (calculated), indicative of a non-coordinative interaction between the nitrogen atom of the N'-substituted amine and the cadmium atom, forming a monomeric 4-coordinated complex. However, the Cd-N_{amine} bond distances were 2.524(9) Å and 2.739(10) Å for [L_bCdBr₂] and [L_cCd(µ-Br)Br]₂, respectively, reflecting a coordination or a coordinative interaction between the nitrogen atom of the N'-substituted amine and the cadmium atom, forming monomeric 5-coordinated [LbCdBr2] and dimeric 6-coordinated [L_cCd(*u*-Br)Br]₂. The average bond lengths of Cd – Br for [L_aCdBr₂] and [L_bCdBr₂] ranged from 2.5230(9) Å to 2.5848(13) Å. In [L_cCd(*µ*-Br)Br]₂, the Cd – $Br_{terminal}$ bond [2.5810(16) Å] was shorter than that of the two Cd-Br_{bridge} bonds [2.7221(13) Å and 2.8415(13) Å]. The angles of $N_{pyrazole} - Cd - N_{pyrazole}$ and Br(1) - Cd - Br(1) in [L_aCdBr₂] were 102.5(2)° and 119.54(4)°, indicative of a distorted tetrahedral geometry. The geometry at the cadmium center in [L_bCdBr₂] was best described as a distorted trigonal bipyramid through coordination of the nitrogen on the cyclohexylmethanamine moiety to the cadmium metal center based on the Cd – N_{amine} bond length of 2.524(9) Å and the bond angles around the cadmium metal. However, [LaCdBr2], which has the same ligand as [L_bCdBr₂], showed a distorted tetrahedral structure without a coordinative interaction of the nitrogen atom of the N'-substituted amine unit and the cadmium atom. It is worth noting that the *yz*-plane of cyclohexyl rings in the cyclohexylmethanamine unit of [LaCdBr2] was distorted by approximately 90° with respect to the *xy*-plane of two pyrazole rings and the cadmium metal center. However, the plane of the cyclohexyl ring and the plane of pyrazole rings and fused metallocyclic rings were

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Scheme 1. Synthesis of ligands and Cd(II) complexes.

almost parallel in [L_bCdBr₂], which contained four bulky methyl groups on two pyrazole rings. Therefore, the parallel or perpendicular orientation of the plane of the cyclohexyl ring with respect to the plane of the pyrazole ring and the substituents attached to the pyrazole ring affected the coordination of the nitrogen of cyclohexylmethanamine to the cadmium metal, thus achieving a 4-coordinated complex [LaCdBr2] and 5-coordinated complex [L_bCdBr₂]. Because the L_c ligand has a coordinative methoxy group in the 3-methoxypropylamine moiety, we expected a monomeric 6-coordinated complex. However, the geometry of $[L_cCd(\mu-Br)Br]_2$ was dimeric distorted octahedral, in which the cadmium metal was coordinated with two pyrazole nitrogen atoms, two bridged bromide atoms, and a terminal bromide atom. This was supported by the Cd – N_{amine} bond length of 2.739(10) Å, indicative of a coordinative interaction between the nitrogen atom of the 3-methoxypropylamine moiety and bonds around the cadmium center, achieving a 6-coordinated geometry of distorted octahedron. However, monomeric [L_bCdBr₂], in which the L_b ligand produces greater steric hindrance than L_c due to the four methyls on the pyrazole rings, exists as a distorted trigonal bipyramid resulting from interactions between the cadmium metal and the nitrogen atom of the cyclohexylmethylamine.

Cd(II) complexes could be activated by cocatalyst modified methylaluminoxane (MMAO) to polymerize methyl methacrylate (MMA), producing poly(methylmethacrylate) (PMMA) [25–30]. The data of PMMA such as tacticity, the number average of molecular weights (M_w) and a glass transition temperature (T_g) are listed in Table 1 [31–33].

Relative to previously reported cobalt(II) complexes with N,Nbis(1H-pyrazolyl-1-methyl)aniline [34], the Cd(II) complexes showed higher molecular weights $(1.20 \times 10^6 \text{ g/mol for } [L_b CdBr_2])$ of syndiotactic PMMA, narrower polydispersity indices (PDI) $(M_w/M_n =$ 1.46 for [L_bCdBr₂]), and similar catalytic activity $(1.13 \times 10^5 \text{ g PMMA})$ mol Cd · h for [L_bCdBr₂]) at 60 °C. The catalytic activity of [L_bCdBr₂] was two-fold higher than that of $[L_aCdBr_2]$ (5.03 × 10⁴ g PMMA/ mol Cd·h). This may be resulted from the increased solubility of [L_bCdBr₂] in toluene due to the four methyl groups on the pyrazole ring moiety, compared to that of [LaCdBr2]. In addition, the steric hindrance may be induced around cadmium metal center in [L_bCdBr₂], resulted from four methyls on the pyrazole rings. In contrast, the catalytic activity of [L_cCd(µ-Br)Br]₂ was also two-fold higher than that of $[L_aCdBr_2]$, however, dimeric $[L_cCd(\mu-Br)Br]_2$ has two active cadmium metals compared to monomeric [LaCdBr2]. Thus, judging from the higher activity of $[L_nCdBr_2]_m$ ($L_n = L_a$, m = 1; L_b , m = 1; L_c , m = 2) than that of reference complex [CdCl₂], which does not contain a ligand coordination complex, the MMA polymerization activity of Cd(II) complexes is more or less associated with the electron density

around the metal center by ligand and the steric factor of the substituents on the pyrazole rings. Syndiotacticity was not sufficiently high to suggest a mechanism of coordination polymerization, but was similar for all Cd(II) complexes (around 70%) and reference **[CdCl₂]**. This also indicated that syndiotacticity was only slightly affected by the substituents on the ligand.

We are now manipulating the substituents on the amine moiety and pyrazole ring to control the formation of diverse coordination modes on cadmium metal.

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Appendix A. Supplementary material

CCDC 983313–983315 contains the supplementary crystallographic data for **[L_aCdBr₂]**, **[L_bCdBr₂]** and **[L_cCdBr₂]**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/ retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. The supplementary spectroscopic data for complexes can be obtained free of charge at http://dx.doi.org/ 10.1016/j.inoche.2014.03.027.

References

- [1] A. John, M.M. Shaikh, R.J. Butcherc, P. Ghosh, Dalton Trans. 39 (2010) 7353.
- [2] D.L. Reger, E.A. Foley, M.D. Smith, Inorg. Chem. 48 (2009) 936.
- [3] F. Calderazzo, U. Englert, C. Hu, F. Marchetti, G. Pampaloni, V. Passarelli, A. Romano, R. Santi, Inorg. Chim. Acta 344 (2003) 197.
- [4] F. Xue, J. Zhao, T.S.A. Hor, Dalton Trans. 40 (2011) 8935.
- [5] F. Xue, J. Zhao, T.S.A. Hor, Dalton Trans. 42 (2013) 5150.
- [6] J. Gätjens, C.S. Mullins, J.W. Kampf, P. Thuéryb, V.L. Pecoraro, Dalton Trans. (2009) 51.
- [7] M.E. Kodadi, F. Malek, R. Touzani, A. Ramdani, Catal. Commun. 9 (2008) 966.
- [8] S.-C. Sheu, M.-J. Tien, M.-C. Cheng, T.-I. Ho, S.-M. Peng, Y.-C. Lin, J. Chem. Soc. Dalton Trans. (1995) 3503.
- [9] M. Espinal, J. Pons, J. García-Antón, X. Solans, M. Font-Bardia, J. Ros, Inorg. Chim. Acta 361 (2008) 2648.
- [10] C. Dowling, V.J. Murphy, G. Parkin, Inorg. Chem. 35 (1996) 2415.
- [11] M.A. Halcrow, Dalton Trans. (2009) 2059.
- [12] M. Guerrero, J. Pons, T. Parella, M. Font-Bardia, T. Calvet, J. Ros, Inorg. Chem. 48 (2009) 8736.
- [13] T. Harit, F. Malek, B.E. Bali, A. Khan, K. Dalvandi, B.P. Marasini, S. Noreen, R. Malik, S. Khan, M.I. Choudhary, Med. Chem. Res. 21 (2012) 2772.
- [14] T. Harit, M. Cherfi, J. Isaad, A. Riahi, F. Malek, Tetrahedron 68 (2012) 4037.
- [15] R. Touzani, A. Ramdani, T. Ben-Hadda, S.E. Kadiri, O. Maury, H.L. Bozec, P.H. Dixneuf, Synth. Commun. 31 (2001) 1315.



Fig. 1. Molecular structure of [L_aCdBr_2]. Selected bond lengths (Å) and angles (°) are Cd(1)–N(3) 3.687, Cd(1)–N(1) 2.217(6), Cd(1)–N(5) 2.230(6), Cd(1)–Br(1) 2.5230(9), Cd(1)–Br(2) 2.5377(10), N(1)–C(1) 1.337(10), N(1)–N(2) 1.353(8), N(2)–C(3) 1.357(10), N(2)–C(4) 1.471(10), C(1)–C(2) 1.372(13), N(1)–Cd(1)–N(5) 102.5(2), N(1)–Cd(1)–Br(1) 104.98(16), N(5)–Cd(1)–Br(1) 107.44(17), N(1)–Cd(1)–Br(2) 111.60(17), N(5)–Cd(1)–Br(2) 109.38(16), Br(1)–Cd(1)–Br(2) 119.54(4), C(1)–N(1)–N(2) 105.1(6), C(1)–N(1)–Cd(1) 126.0(5), N(2)–N(1)–Cd(1) 128.6(5), N(1)–N(2)–C(3) 111.4(7).

- [16] S. Bhattacharyya, S.B. Kumar, S.K. Dutta, E.R.T. Tiekink, M. Chaudhury, Inorg. Chem. 35 (1996) 1967.
- [17] K. Li, J. Darkwa, I.A. Guzei, S.F. Mapolie, J. Organomet. Chem. 660 (2002) 108.
- [18] S. Tsuji, D.C. Swenson, R.F. Jordan, Organometallics 18 (1999) 4758.
- [19] L.L. de Oliveira, R.R. Campedelli, M.C.A. Kuhn, J.-F. Carpentier, O.L. Casagrande Jr., J. Mol. Catal. A: Chem. 288 (2008) 58.
- [20] W.L. Driessen, Recl. Trav. Chim. Pays-Bas 101 (1982) 441.
- [21] J.-H. Liu, X.-Y. Wu, Q.-Z. Zhang, X. He, W.-B. Yang, C.-Ź. Lu, J. Coord. Chem. 60 (2007) 1373.
- [22] J. Pons, J. Garcia-Anton, M. Font-Bardia, T. Calvet, J. Ros, Inorg. Chim. Acta 362 (2009) 2698.
- [23] C. Hopa, M. Alkan, C. Kazak, N.B. Arslan, R. Kurtaran, J. Chem. Crystallogr. 40 (2010) 160.
 [24] P.M. van Berkel, W.L. Driessen, R. Hamalainen, J. Reedijk, U. Turpeinen, Inorg. Chem. 33 (1994) 5920.
- [25] C. Cui, A. Shafir, C.L. Reeder, J. Arnold, Organometallics 22 (2003) 3357.
- [26] T.V. Laine, U. Piironen, K. Lappalainen, M. Klinga, E. Aitola, M. Leskela, J. Organomet. Chem. 606 (2000) 112.
- [27] Y.-B. Huang, G.-R. Tang, G.-Y. Jin, G.-X. Jin, Organometallics 27 (2008) 259.
- [28] G. Tang, G.-X. Jin, Dalton Trans. (2007) 3840.
- [29] C. Carlini, M. Martinelli, E. Passaglia, A.M.R. Galletti, G. Sbrana, Macromol. Rapid Commun. 22 (2001) 664.
- [30] Y.-J. Hu, H.H. Zou, M.-H. Zeng, N.S. Weng, J. Organomet. Chem. 694 (2009) 366.
- [31] T. Kitaura, T. Kitayama, Macromol. Rapid Commun. 28 (2007) 1889.
- [32] Freeman, S.M. Howdle, Macromolecules 37 (2004) 6667.
- [33] I.A. Opeida, M.A. Kompanets, O.V. Kushch, E.S. Papayanina, Theor. Exp. Chem. 47 (2011) 30.
- [34] M. Yang, W.J. Park, K.B. Yoon, J.H. Jeong, H. Lee, Inorg. Chem. Commun. 14 (2011) 189.



Fig. 2. Molecular structure of [L_bCdBr₂]. Selected bond lengths (Å) and angles (°) are Cd(1) – N(3) 2.524(9), Cd(1) – N(1) 2.380(8), Cd(1) – N(5) 2.382(8), Cd(1) – Br(2) 2.5309(12), Cd(1) – Br(1) 2.5848(13), N(1) – C(1) 1.329(12), N(1) – N(2) 1.362(11), N(2) – C(3) 1.351(13), N(2) – C(4) 1.451(12), C(1) – C(2) 1.414(15), N(1) – Cd(1) – N(5) 138.9(3), N(1) – Cd(1) – N(3) 69.3(3), N(5) – Cd(1) – N(3) 70.3(3), N(1) – Cd(1) – Br(2) 101.77(19), N(5) – Cd(1) – Br(2) 101.37(18), N(3) – Cd(1) – Br(2) 135.68(17), N(1) – Cd(1) – Br(1) 102.0(2), N(5) – Cd(1) – Br(1) 94.95(19), N(3) – Cd(1) – Br(1) 103.87(17), Br(2) – Cd(1) – Br(1) 120.37(5).



Fig. 3. Molecular structure of $[L_cCd(\mu-Br)Br]_2$. Selected bond lengths (Å) and angles (°) are Cd(3)-N(3) 2.739(10), Cd(1)-N(1) 2.295(8), Cd(1)-N(5) 2.338(9), Cd(1)-Br(2) 2.5810(16), Cd(1)-Br(1) 2.7221(13), Cd(1)-Br(1#) 2.8415(13), N(1)-C(1) 1.328(13), N(1)-N(2) 1.341(13), N(2)-C(3) 1.356(14), N(2)-C(4) 1.459(14), C(1)-C(2) 1.410(16), N(1)-Cd(1)-N(5) 90.6(3), N(1)-Cd(1)-Br(2) 97.2(2), N(5)-Cd(1)-Br(2) 94.6(2), N(1)-Cd(1)-Br(1) 156.1(2), N(5)-Cd(1)-Br(1) 90.7(2), Br(2)-Cd(1)-Br(1) 106.42(4), N(1)-Cd(1)-Br(1#) 84.6(2), N(5)-Cd(1)-Br(1#) 161.8(2), Br(2)-Cd(1)-Br(1#) 103.44(4), Br(1)-Cd(1)-Br(1#) 86.77(4).

Table 1

Polymerization of MMA by Cd(II) complexes in the presence of MMAO.

Entry	Catalyst ^a	Yield ^b (%)	Activity ^c \times 10 ⁴ (g/mol C at \cdot h)	T_g (°C)	%mm	Tacticiy %mr	%rr	$M_w{}^d \times 10^5 (g/mol)$	M_{w}/M_n
1	[CdCl ₂] ^e	22.6	3.53	123	5.60	30.3	64.1	4.72	1.49
2	MMAO ^f	8.97	1.40	120	37.2	10.9	51.9	6.78	2.09
3	$[L_1CdBr_2]$	32.3	5.03	121	6.90	22.9	70.2	7.73	2.16
4	$[L_2CdBr_2]$	72.4	11.3	124	6.20	25.5	68.3	12.0	1.46
5	$[L_3Cd(\mu-Br)Br]_2$	66.2	10.3	123	6.70	24.8	68.5	8.75	2.00

 $^a~[Cd(II)~catalyst]_0=15~\mu mol,~[MMA]_0/[MMAO]_0/[Cd(II)~catalyst]_0=3100:500:1.$

^b Yield defined a mass of dried polymer recovered/mass of monomer used.

^c Activity is calculated as (g PMMA)/(mol Cd · h) at 60 °C.

^d Determined by gel permeation chromatography (GPC) eluted with THF at room temperature by filtration with polystyrene calibration.

^e It is a blank polymerization in which anhydrous [CdCl₂] was also activated by MMAO.

^f It is a blank polymerization which was done solely by MMAO.