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Solution structure of cadmium carboxylate and its implications for the synthesis of cadmium chalcogenide nanocrystals[†]

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Diffusion-ordered spectroscopy (DOSY) was used to investigate the solution structure of cadmium carboxylate. The molecular weights of cadmium complexes highly depend on the solvent; the complexes are polymeric in toluene but break up in the presence of polar solvents or coordinating ligands.

CdE (E = S, Se, Te) nanocrystals have made a great impact in many technological applications.^{1–4} Over the last two decades, a large number of synthetic methods have been developed to prepare these materials,^{5–8} and significant efforts have been devoted to understand the mechanism of nanocrystal formation in order to improve the control over its size, shape, and composition.^{9–11} The fate of the chalcogenide sources was the subject of several recent studies. Both phosphine chalcogenide^{12,13} and dissolved S and Se in octadecene¹⁴ or amines^{15,16} have received significant attention. In contrast, not much is known about the solution structure and reactivity of cadmium precursors, not to mention their role in nanocrystal synthesis.

The solution structure of the cadmium precursor could affect the precursor-conversion kinetics and consequently the nucleation and growth kinetics of nanocrystals. The Lewis acidity of the cadmium precursor is known to significantly affect the rate of monomer production in phosphine-based syntheses.^{17–19} This fact raises the question of whether other structural variations, such as degree of polymerization and coordination of Cd²⁺, could also affect the reactivity and if so, to what degree. In addition, the cadmium precursor may also directly impact the growth of nanocrystals by acting as a template. For example, a lamellar mesophase of Cd(OAc)2 or CdCl2 layers separated by n-octylamine bi-layers was proposed to be responsible for the formation of planar CdSe nanostructures by Hyeon and Buhro groups.²⁰⁻²² A clear understanding of the solution structure of cadmium carboxylate could clarify their roles in the nanocrystal synthesis and may lead to new synthetic methodologies.

A major challenge in studying the solution structure of cadmium carboxylate is the lack of suitable characterization techniques. Cd²⁺ ions can have a wide range of coordination numbers and diverse geometries. In the solid state, cadmium carboxylates tend to form coordination polymers^{11,23,24} and break down to smaller complexes in the presence of a coordinating ligand.^{25,26} Although it is reasonable to assume that the solution species should have a similar structure to that found in the solid state, it is equally conceivable that the polymeric structure could be disrupted by solvent or ligand binding. Unfortunately, conventional characterization tools (e.g., mass spectrometry and FTIR) could not provide quantitative information about the nature of the metal coordination and degree of polymerization in solution. For example, mass spectrometry is known to underestimate the concentration of large molecular weight species and often requires polar solvents (e.g., for electrospray) and/or additives that could affect the structure of cadmium complexes. To the best of our knowledge, the solution structure of cadmium carboxylate has not been established.

Herein we report a study of the solution structure of cadmium carboxylate using ¹¹³Cd and ¹H DOSY. DOSY is a pseudo-2D NMR technique that measures diffusion coefficients, which in turn can be used to estimate the hydrodynamic radii and formula weight of the molecule.^{27,28} ¹H-DOSY has been employed to estimate the particle size of II–VI and IV–VI nanocrystals and to study the presence of ligands and the interaction of ligands with the nanocrystal surface.^{29,30}

A major goal of this study is to address two long-standing questions that are fundamental to the reaction mechanism of CdE nanocrystals: (1) what is the molecular weight of cadmium carboxylate in solution? (2) What is the coordination environment of the Cd center? In particular, are the carboxylate ligands labile when dissolved in solution? Our result shows that cadmium carboxylate exists as a polymer in toluene and the formula weight (FW) decreases in the presence of a coordinating ligand or polar solvent. However, even in the latter case, ¹H and ¹¹³Cd DOSY experiments revealed similar diffusion coefficients suggesting that there is no dissociation of carboxylate from Cd²⁺ (*vide infra*).³¹

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Fig. 1 (above) ¹H DOSY and natural abundance ¹¹³Cd DOSY of Cd(OAc)₂·2H₂O dissolved in octylamine. Note that the acetate resonance of Cd(OAc)₂ in the ¹H DOSY diffuses with the same diffusion coefficient (1.78 × 10⁻¹⁰ m² s⁻¹) as the one observed in the ¹¹³Cd DOSY (1.79 × 10⁻¹⁰ m² s⁻¹). (below) ¹H DOSY of Cd(OAc)₂·2H₂O dissolved in octylamine in the presence of polystyrene (M_w = 2400) and di-*tert*-butylbiphenyl (M_w = 266.42) added as two inert internal references.

Our first model system is cadmium acetate, Cd(OAc)2, a commonly used cadmium precursor for the synthesis of CdSe nanostructures and clusters.^{21,32-35} Cd(OAc)₂ is known to form coordination polymers in the solid state²³ and is not soluble in non-polar organic solvents. It is soluble in coordinating solvents such as methanol and octylamine. We studied the behavior of Cd(OAc)2·2H2O dissolved in octylamine under similar conditions to those employed in the synthesis of planar CdSe nanostructures.^{21,22} The solution in octylamine exhibited a single sharp signal in the ¹¹³Cd NMR spectrum at 154.6 ppm (see Fig. S1 (ESI⁺), referenced externally to 0.1 M Cd(ClO₄)₂ in D₂O). No reaction between octylamine and acetate was observed (see the ESI,[†] Fig. S2-S4). The ¹H DOSY spectrum (Fig. 1 and Fig. S5, ESI[†]) showed two markedly different diffusion coefficients for octylamine ($D = 6.00 \times$ $10^{-10}~\text{m}^2~\text{s}^{-1})$ and acetate (1.78 $\times~10^{-10}~\text{m}^2~\text{s}^{-1})$. The diffusion coefficient (1.79 \times 10^{-10} m 2 s $^{-1}$) extracted from ^{113}Cd DOSY (Fig. 1 and Fig. S5, ESI⁺) matched perfectly with the one for acetate extracted from ¹H DOSY. Although this result strongly suggests that acetate groups are tightly bound to the Cd²⁺ centers, the formation of ion pairs cannot be ruled out since it would also result in the observation of the same diffusion coefficient in the ¹H and ¹¹³Cd DOSY experiments. We note that exchange of carboxylate from Cd²⁺ in aqueous solution is known to be fast on the NMR time scale.³¹ The FW of the Cd complex was estimated to be 799 (see the ESI,[†] Table S1 and Fig. S6, for the calculation of the FW), consistent with a small complex. Given that monomeric complexes of the type $Cd(OAc)_2(octylamine)_x$ have a FW = 488.99 and 747.47 for x = 2 and 4 respectively, the formation of species larger than a dimer seems less likely.

To study the structure of cadmium carboxylate in a noncoordinating solvent, we chose cadmium oleate, $Cd(OA)_2$ for its wide application in nanocrystal synthesis.^{5,18,36} Our $Cd(OA)_2$ sample was prepared by reacting CdO and oleic acid (HOA). The crude reaction mixture was precipitated by adding acetone in order to remove excess of free HOA (see the ESI,[†] for experimental details and Fig. S7 and S8). When a sample of $Cd(OA)_2$ was dissolved in toluene a viscous solution was obtained, and the ¹H NMR line widths of the oleate ligand are considerably broader than the residual toluene solvent signals (Fig. S8–S10, ESI[†]). This observation is in contrast to the sharp NMR resonance observed for $Cd(OA)_2$ in octylamine. In addition, we also observed strong, negative NOEs in the ¹H–¹H NOESY spectrum (Fig. S11, ESI[†]), characteristic of slowly tumbling molecules.³⁰ These two facts suggest a polymeric structure for $Cd(OA)_2$ when dissolved in toluene.

In this case, ¹¹³Cd DOSY was challenging because of the broad line width (Fig. S10, ESI[†]). However, given that toluene is neither coordinating nor polar and the fact that Cd(OAc)₂ does not dissociate in octylamine we expect the dissociation of the oleate ligand to be minimal in toluene (vide infra). Fig. 2 shows the ¹H DOSY spectrum of this sample collected with three internal standards (Table S2, ESI⁺). We estimated that the FW of this Cd(OA)₂ sample was 20 650 (see the ESI,[†] Fig. S12 and Table S3, for details regarding the calculation of the FW and also Table S4 for control experiments using polystyrene standards), which translates to 30.5 units of Cd(OA)₂. We note that there are other important factors that can impact the exact structure of the metal carboxylate in solution, such as concentration, temperature, and presence of adventitious water. For example, we found that the FW obtained for Cd(OA)₂ in toluene was highly dependent on the preparation of the sample, and could fluctuate between 13000 and 40000. Further studies are being carried out to probe the dependence of the FW on the synthesis and purification conditions.

Many nanocrystal syntheses are conducted in a non-coordinating solvent but in the presence of reagents or ligands that can coordinate to Cd. Therefore, it is important to understand how these molecules affect the structure of cadmium carboxylate. To this end, we have measured the diffusion coefficients of Cd(OA)₂ in toluene in the presence of three model ligands: SePMe₃, OPMe₃, and octylamine.^{16,21,33} We observed that the addition of ligand sharpened



Fig. 2 ¹H DOSY spectrum of Cd(OA)₂ dissolved in toluene at 300 K in the presence of three internal references: polystyrene ($M_w = 13200$), polydimethylsiloxane (DMS, $M_w = 28500$) and Poly(methyl methacrylate) (MMA, $M_w = 68500$). Shape of the signal at 2.09 ppm is due to overlapping toluene resonance. See the ESI† (Table S3) for diffusion coefficients for each of the species.



Fig. 3 FW of $Cd(OA)_2$ (toluene-d₈ solution) in the presence of different amount of ligands.

the oleate resonances and increased the diffusion coefficient of $Cd(OA)_2$ (Fig. S13–S15, ESI[†]), suggesting that the degree of oligomerization of $Cd(OA)_2$ was reduced. As shown in Fig. 3, the addition of just 1.5 equivalents of octylamine decreased the FW of $Cd(OA)_2$ in toluene from 23 500 to 2499. Subsequent additions of octylamine slightly and progressively reduce its FW to 1985 after the addition of 9 equivalents. Similar observations were made with SePMe₃ and OPMe₃ (see Fig. 3 and the ESI,[†] Tables S5 and S6 and Fig. S16).

In the presence of excess ligands, the FW calculated approaches a monomeric or dimeric type $[Cd(OA)_2(L)_x]$. Additional support for the formation of such complexes comes from 2D-NOESY and 2D-ROESY spectra of a mixture of $Cd(OA)_2$ and 2 equivalents of octylamine, both of which showed that the α -CH₂ protons of oleate and octylamine are close to each other in space (see the ESI,† Fig. S17–S21 for details). This result indicates that octylamine and oleate ligands are simultaneously coordinated to cadmium. Finally, the fact that SePMe₃ also breaks up the polymeric structure of cadmium oleate suggests that the nucleophilic attack of carboxylate on SePMe₃ must occur in a small cadmium complex, close to a monomer or dimer, rather than in a polymeric one.^{9,13} In a similar vein, the supramolecular structures observed by Buhro and coworkers^{20–22} are likely constructed from and in equilibrium with fast diffusing small complexes (see the ESI,† Scheme S1 for details).

In conclusion, we have used ¹H and ¹¹³Cd DOSY to study the solution structure of two cadmium carboxylate complexes under conditions similar to those used in a wide range of low temperature nanocrystal syntheses.^{16,21,22,37–39} The structure was found to be polymeric in pure toluene and monomeric or dimeric in the presence of excess ligands such as octylamine, SePMe₃ or OPMe₃. Our result indicated that the dominant cadmium species during nanocrystal synthesis are small complexes and not polymeric ones.^{9,13} While the effect of ligands on nanocrystal growth and shape control has been well documented, our results showed that ligands also affect the nature of the cadmium precursor. With a detailed understanding of the cadmium precursor, we hope future work will develop more realistic kinetic analysis and theoretical modelling of the effect of ligands on nanocrystal synthesis.

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Notes and references

- V. I. Klimov, A. A. Mikhailovsky, S. Xu, A. Malko, J. A. Hollingsworth, C. A. Leatherdale, H. J. Eisler and M. G. Bawendi, *Science*, 2000, 290, 314.
- 2 W. U. Huynh, J. J. Dittmer and A. P. Alivisatos, Science, 2002, 295, 2425.
- 3 G. Han, T. Mokari, C. Ajo-Franklin and B. E. Cohen, J. Am. Chem. Soc., 2008, 130, 15811.
- 4 S. Coe, W.-K. Woo, M. Bawendi and V. Bulovic, *Nature*, 2002, **420**, 800.
- 5 W. W. Yu and X. Peng, Angew. Chem., Int. Ed., 2002, 41, 2368-2371.
- 6 Y. C. Cao and J. Wang, J. Am. Chem. Soc., 2004, 126, 14336-14337.
- 7 J. Joo, H. B. Na, T. Yu, J. H. Yu, Y. W. Kim, F. Wu, J. Z. Zhang and T. Hyeon, *J. Am. Chem. Soc.*, 2003, **125**, 11100.
- H. Zhang, B.-R. Hyun, F. W. Wise and R. D. Robinson, *Nano Lett.*, 2012, 12, 5856.
- 9 H. Liu, J. S. Owen and A. P. Alivisatos, J. Am. Chem. Soc., 2007, 129, 305.
- 10 C. M. Evans, M. E. Evans and T. D. Krauss, J. Am. Chem. Soc., 2010, 132, 10973.
- 11 R. Garcia-Rodriguez, M. P. Hendricks, B. Cossairt, H. Liu and J. S. Owen, *Chem. Mater.*, 2013, **25**, 1233.
- 12 T. P. A. Ruberu, H. R. Albright, B. Callis, B. Ward, J. Cisneros, H.-J. Fan and J. Vela, *ACS Nano*, 2012, **6**, 5348–5359.
- 13 R. Garcia-Rodriguez and H. Liu, J. Am. Chem. Soc., 2012, 134, 1400-1403.
- 14 C. Bullen, E. J. van, J. Jasieniak, J. E. Cosgriff, R. J. Mulder, E. Rizzardo, M. Gu and C. L. Raston, *Chem. Mater.*, 2010, 22, 4135–4143.
- 15 J. W. Thomson, K. Nagashima, P. M. Macdonald and G. A. Ozin, J. Am. Chem. Soc., 2011, 133, 5036-5041.
- 16 Z. Li, Y.-J. Ji, R. Xie, S. Y. Grisham and X.-G. Peng, J. Am. Chem. Soc., 2011, 133, 17248–17256.
- 17 F. Wang and W. E. Buhro, J. Am. Chem. Soc., 2012, 134, 5369-5380.
- 18 W. W. Yu, Y. A. Wang and X. Peng, Chem. Mater., 2003, 15, 4300-4308.
- 19 Z. A. Peng and X. Peng, J. Am. Chem. Soc., 2001, 123, 1389-1395.
- 20 J. S. Son, X.-D. Wen, J. Joo, J. Chae, S.-i. Baek, K. Park, J. H. Kim, K. An, J. H. Yu, S. G. Kwon, S.-H. Choi, Z. Wang, Y.-W. Kim, Y. Kuk, R. Hoffmann and T. Hyeon, *Angew. Chem., Int. Ed.*, 2009, **48**, 6861.
- 21 Y.-H. Liu, F. Wang, Y. Wang, P. C. Gibbons and W. E. Buhro, J. Am. Chem. Soc., 2011, 133, 17005.
- 22 Y. Wang, Y.-H. Liu, Y. Zhang, F. Wang, P. J. Kowalski, H. W. Rohrs, R. A. Loomis, M. L. Gross and W. E. Buhro, *Angew. Chem., Int. Ed.*, 2012, **51**, 6154.
- 23 W. Harrison and J. Trotter, J. Chem. Soc., Dalton Trans., 1972, 956.
- 24 L. Poul, M. Fakhfakh, M. Taibi, N. Jouini, P. Herson and F. Fievet, *J. Chem. Crystallogr.*, 2005, **35**, 285.
- 25 S. M. Vickers, P. D. Frischmann and M. J. MacLachlan, *Inorg. Chem.*, 2011, 50, 2957.
- 26 K. Bania, N. Barooah and J. B. Baruah, Polyhedron, 2007, 26, 2612.
- 27 D. Li, I. Keresztes, R. Hopson and P. G. Williard, Acc. Chem. Res., 2009, 42, 270.
- 28 D. Li, G. Kagan, R. Hopson and P. G. Williard, J. Am. Chem. Soc., 2009, 131, 5627.
- 29 I. Moreels, B. Fritzinger, J. C. Martins and Z. Hens, *J. Am. Chem. Soc.*, 2008, **130**, 15081.
- 30 Z. Hens and J. C. Martins, Chem. Mater., 2013, 25, 1211.
- 31 K. H. Chung and C. H. Moon, J. Chem. Soc., Dalton Trans., 1996, 75.
- 32 Z. H. Sun, H. Oyanagi, H. Nakamura, Y. Jiang, L. Zhang, M. Uehara, K. Yamashita, A. Fukano and H. Maeda, *J. Phys. Chem. C*, 2010, 114, 10126.
- 33 N. Pradhan, H. Xu and X. Peng, Nano Lett., 2006, 6, 720.
- 34 Y.-H. Liu, V. L. Wayman, P. C. Gibbons, R. A. Loomis and W. E. Buhro, *Nano Lett.*, 2010, **10**, 352.
- 35 K. Yu, Adv. Mater., 2012, 24, 1123.
- 36 C. R. Bullen and P. Mulvaney, Nano Lett., 2004, 4, 2303.
- 37 B. M. Cossairt and J. S. Owen, Chem. Mater., 2011, 23, 3114.
- 38 S. Kudera, M. Zanella, C. Giannini, A. Rizzo, Y. Li, G. Gigli, R. Cingolani, G. Ciccarella, W. Spahl, W. J. Parak and L. Manna, *Adv. Mater.*, 2007, **19**, 548.
- 39 J. C. Newton, K. Ramasamy, M. Mandal, G. K. Joshi, A. Kumbhar and R. Sardar, J. Phys. Chem. C, 2012, **116**, 4380.