Carbon dioxide activation: synthesis and characterization of a cadmium(II) dinuclear complex with a novel μ-carbonato bridge

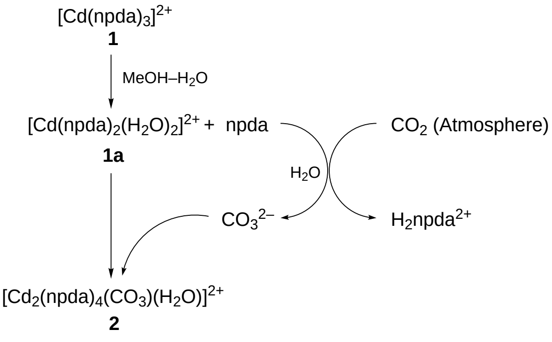
Chandi Pariya,[*a†] **Vedavati G. Puranik**[b] **and Nirmalendu Ray Chaudhuri**[*a‡]

[a] *Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032, India*
[b] *Division of Physical Chemistry, National Chemical Laboratory, Pune 411 008, India*

The cadmium(II) complex of *N′*-isopropyl-2-methylpropane-1,2-diamine (npda), [Cd(npda)$_3$][ClO$_4$]$_2$ 1 in aqueous methanol absorbs CO_2 from air to form a cadmium(II) dinuclear complex, [Cd(npda)$_4$(CO$_3$)(H$_2$O)][ClO$_4$]$_2$·H$_2$O 2, the first ever example of a μ-carbonato cadmium(II) diamine complex which is characterized by elemental analysis, IR and crystal structure determination.

Transition metals bound to CO_2 and reactions of the resulting complexes have been of much interest in connection with utilization of CO_2.[1–3] A large-scale method of reducing CO_2 similar to photosynthesis in green plants, has, as yet, not been developed. The benefit of reduction of CO_2 in the atmosphere can be doubled if CO_2 can be absorbed and harvested as a chemical feedstock.[4,5] Development of metal–CO_2 chemistry derived much of its inspiration from such a challenging possibility. However, most prepared and characterized transition-metal complexes containing CO_2[6–12] and a variety of bridging carbonates[13–17] are air-sensitive. Here we describe: (*a*) the first example of a cadmium complex which can spontaneously react with CO_2 under atmospheric conditions in the presence of a base, and (*b*) structural characterization of the resultant dinuclear complex featuring a novel μ-carbonato group bridging two cadmium ions.

In the course of our studies[18–21] on the synthesis, characterization and thermal investigation of transition-metal (nickel, copper, zinc and cadmium) complexes of *N′*-isopropyl-2-methylpropane-1,2-diamine (npda), we reported[20] that only cadmium(II) perchlorate generates tris-diamine species with excess npda, [Cd(npda)$_3$][ClO$_4$]$_2$ **1** being obtained as a white powder. When a methanolic solution of **1** was stirred in air and its volume reduced, colourless crystals formulated as [Cd$_2$(npda)$_4$(CO$_3$)(H$_2$O)][ClO$_4$]$_2$·H$_2$O **2** were obtained in good yield.[§] Complex **2** was also prepared from [Cd(npda)$_3$][ClO$_4$]$_2$ by passing a stream of carbon dioxide or by addition of carbonate in methanolic solution. The ease of formation of this unusual bimetallic complex may be attributed to the unique steric features of npda, since no effort was made to promote reaction with CO_2, nor has such bridging been observed previously for other cadmium complexes featuring different ligands.



Scheme 1

Complex **2** gave satisfactory elemental analysis and its IR spectrum showed the presence of amine as well as carbonate[16] groups, the latter being absent in **1**. The tris-diamine complex **1**, when dissolved in an aqueous medium, dissociates into [Cd(npda)$_2$(H$_2$O)$_2$][ClO$_4$]$_2$ **1a**[20b] and npda, to release the excessive steric congestion owing to the bulky substituents of a third npda ligand. It appears that complex **1a** is a very active species for reaction with CO_2 in the presence of npda; the latter is supposed to act also as a base, which would raise the concentration of CO_2 in solution. Although at a first glance it might appear that the complex **2** is generated by the interaction of the bis-complex and CO_2 as the metal : npda ratio in **2** was 1 : 2, the formation of **2** from a simple bis-complex was not observed. The proposed mechanistic pathway for this reaction is shown in Scheme 1.

The initial loss of a ligand unit leads to a coordinatively unsaturated intermediate, [Cd(npda)$_2$]$^{2+}$ which coordinates to two molecules of water to form [Cd(npda)$_2$(H$_2$O)$_2$]$^{2+}$. The released npda reacts with CO_2 to form CO_3^{2-} [$CO_2 + H_2O + \text{npda} \rightarrow CO_3^{2-}\ (aq) + H_2\text{npda}^{2+}$] and eventually yields [Cd$_2$(npda)$_4$(CO$_3$)(H$_2$O)]$^{2+}$.[14]

The crystal structure of **2** revealed the presence of a novel, bridging tridentate carbonate, and presented an excellent opportunity to study the configuration and interactions of the two npda ligands in an octahedral configuration. Fig. 1 shows a view and atom-numbering scheme of the dication [Cd$_2$(npda)$_4$(CO$_3$)(H$_2$O)]$^{2+}$ containing a novel μ-carbonato bridge, which is associated in the crystal with two perchlorate ions and a water molecule of crystallization.

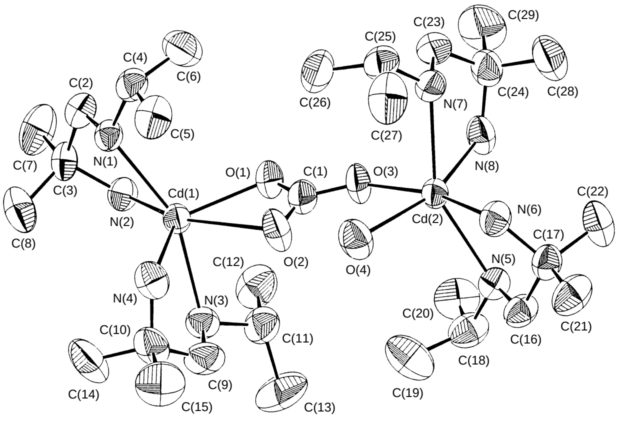


Fig. 1 ORTEP diagram of complex **2**. Thermal elipsoid are drawn at 50% probability, the water molecule and perchlorate ions are not shown for clarity. Selected bond distances (Å) and angles (°): Cd(1)–O(1) 2.172(4), Cd(1)–O(2) 2.768(4), Cd(1)–N(1) 2.389(4), Cd(1)–N(2) 2.324(4), Cd(1)–N(3) 2.407(5), Cd(1)–N(4) 2.324(4), Cd(2)–O(3) 2.238(3), Cd(2)–O(4) 2.351(4), Cd(2)–N(5) 2.385(5), Cd(2)–N(6) 2.386(4), Cd(2)–N(7) 2.403(5), Cd(2)–N(8) 2.309(4), C(1)–O(1) 1.278(6), C(1)–O(2) 1.279(7), C(1)–O(3) 1.268(6); O(1)–Cd(1)–O(2) 51.46(3), O(3)–Cd(2)–O(4) 82.8(2), N(2)–Cd(1)–N(1) 75.0(2), N(4)–Cd(1)–N(3) 75.8(2), N(5)–Cd(2)–N(6) 75.0(2), N(8)–Cd(2)–N(7) 73.7(2), O(1)–C(1)–O(2) 119.7(4), O(1)–C(1)–O(3) 118.7(5), O(2)–C(1)–O(3) 121.6(5).

In the dinuclear complex cation both cadmium atoms have a significantly distorted octahedral coordination with N_4O_2 chromophores. Distortions from ideal octahedral geometry are due to the two bidentate diamines and the asymmetric nature of the bridging carbonato ion, the smallest *cis* angle being 51.46(3)° [O(1)–Cd(1)–O(1)]. The carbonato moiety is planar and the C–O bond distances are almost equal [av. 1.278(6) Å] unlike those in bidentate carbonate systems.[17] A three-dimensional network of intra- and inter-molecular hydrogen bonds involving water molecules, amine nitrogen atoms and perchlorate ions stabilizes the crystal packing; the shortest hydrogen bond is $O(1w)\cdots O(1)$ $(1 + x, y, z)$ 2.812(3) Å.

We thank Dr A. Sarkar, Division of Organic Chemistry (Synthesis), National Chemical Laboratory, Pune for helpful discussions and also Professor T. P. Singh, All India Institute of Medical Science, New Delhi is acknowledged for preliminary data (complex **2**) on the crystal structure determination. One of us (C. P.) thanks Professor Chung-Sun Chung, Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan, ROC for encouragement.

Footnotes

† Present address: Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 30043, ROC.
E-mail: pariya@chem.nthu.edu.tw

‡ E-mail: icnrc@iacs.ernet.in

§ *X-Ray structure determination*: a colourless crystal of approximate dimensions 0.2 × 0.3 × 0.6 mm was used for the data collection on a PC controlled Enraf-Nonius CAD-4 single-crystal X-ray diffractometer (293 K) with graphite-monochromated Mo-Kα radiation using ω–2θ scan mode and 1° $\min^{-1}$ scan speed. Unit-cell parameters were refined from 25 least-squares fitted machine-centred reflections in the range $18 < 2\theta < 30°$. Three standard reflections measured every hour showed $<4\%$ variation in intensity. The structure was solved by direct methods using NRCVAX[22] and refined by full-matrix least-squares techniques on F^2 using SHELXL-93[23] to $R = 0.0280$, $R_w = 0.075$ from 5358 unique reflections, from a total number of 5558 reflections collected. Least-squares refinement of scale, position and anisotropic thermal parameters for non-hydrogen atoms was carried out. The hydrogen-atom positions were geometrically fixed and confirmed by difference Fourier analysis. Each hydrogen atom was assigned the same isotropic thermal parameter as the atom to which it was bonded.

Crystal data for **2**: $C_{29}H_{76}Cd_2Cl_2N_8O_{13}$, $M = 1036.6$, monoclinic, space group $P2_1$, $a = 9.338(8)$, $b = 12.888(1)$, $c = 20.493(3)$ Å, $\beta = 101.78(4)°$, $U = 2414(2)$ Å^3, $Z = 2$, $D_c = 1.426$ Mg m^{-3}. Final R $[I > 2\sigma(I)]$ $R_1 = 0.0280$ and $R_w = 0.0754$; $w = 1/\sigma^2[(F_o^2) + (0.0499p)^2 + 0.6831p]$, where $p = (F_o^2 + 2F_c^2)/3$. Number of refined parameters is 486. The 'Flack parameter' is 0.083(3).[24] CCDC 510.

References

1 D. J. Darensbourg and R. Kuetosic, *Adv. Organomet. Chem.*, 1983, **22**, 129; D. A. Palmer and R. V. Eldik, *Chem. Rev.*, 1983, **83**, 651; R. Eisenberg and D. E. Hendricksen, *Adv. Catal.*, 1979, **28**, 79.

2 T. Ito and A. Yamamto, *Organic and Bio-organic Chemistry of Carbon Dioxide*, ed. S. Inoue and S. Yamazaki, Wiley, New York, 1980; J. Cramer and A. L. Meyers, *Atmos. Environ.*, 1972, **6**, 563; C. F. Base, Jr., H. E. Goeller, J. S. Oison and R. M. Rotty, *Am. J. Sci.*, 1977, **65**, 310.

3 J. R. Bolton, *Science*, 1978, **202**, 705; R. William, R. S. Bloom and A. Bloom, *Appl. Phys. Lett.*, 1978, **33**, 381.

4 A. Naitoh, K. Otha, T. Mizuno, H. Yoshida, M. Sakai and H. Noda, *Electrochim. Acta*, 1993, **38**, 2177.

5 J. Costamagna, G. Ferraudi, J. Canales and J. Vargas, *Coord. Chem. Rev.*, 1996, **148**, 221.

6 M. Aresta, C. F. Nobile, V. G. Albano, E. Forni and M. Manassero, *J. Chem. Soc., Chem. Commun.*, 1975, 636; M. Aresta and C. F. Nobile, *J. Chem. Soc., Dalton Trans.*, 1977, 708.

7 S. Gambarotta, F. Arena, C. Floriani and P. F. Zanazzi, *J. Am. Chem. Soc.*, 1982, **104**, 5082.

8 G. S. Bristow, P. B. Hitchcock and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 1981, 1145.

9 J. C. Calabrese, T. Herskovitz and J. B. Kinney, *J. Am. Chem. Soc.*, 1983, **105**, 5914.

10 S. Gambarotta, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Am. Chem. Soc.*, 1985, **107**, 2985; R. Alvarez, E. Carmona, J. M. Marin, M. L. Poveda, E. Gutierrez-Puebla and A. Monge, *J. Am. Chem. Soc.*, 1986, **108**, 2286.

11 B. Demerseman, R. Mahé and P. H. Dixneuf, *J. Chem. Soc., Chem. Commun.*, 1984, 1394.

12 M. Kato and T. Ito, *Inorg. Chem.*, 1985, **24**, 509.

13 S. Cenini, F. Porta, M. Pizzotti and C. Crotti, *J. Chem. Soc., Dalton Trans.*, 1985, 163; H. H. Karsch, *Chem. Ber.*, 1977, **210**, 2213.

14 This type of mechanism was originally proposed by Tanase *et al.* in $[Ni(Me_2en)_3](ClO_4)_2$ (Me_2en = *N,N*-dimethylethane-1,2-diamine) where the final complex was $[Ni_3(Me_2en)_6(CO_3)(H_2O)_4][ClO_4]_4$; T. Tanase, S. Nitta, S. Yoshikawa, K. Kobayashi, T. Sakurai and S. Yano, *Inorg. Chem.*, 1992, **31**, 1058.

15 S. C. Rawle, C. J. Harding, P. Moore and N. W. Alcock, *J. Chem. Soc., Chem. Commun.*, 1992, 1701.

16 E. Carmona, F. Gonzalez, M. L. Poveda, J. M. Marin, J. L. Atwood and R. D. Rogers, *J. Am. Chem. Soc.*, 1983, **105**, 3365.

17 R. J. Geue and M. R. Snow, *J. Chem. Soc., A*, 1971, 2981; M. R. Churchill, G. M. Harris, R. A. Lashewycz, T. P. Dasgupta and K. Koshy, *Inorg. Chem.*, 1979, **18**, 2290.

18 C. Pariya, A. Ghosh and N. Ray Chaudhuri, *J. Chem. Res.* (*S*), 1994, 428; C. Pariya, S. Ghosh, A. Ghosh, M. Mukherjee, A. K. Mukherjee and N. Ray Chaudhuri, *J. Chem. Soc., Dalton Trans.*, 1995, 337; C. Pariya, A. Ghosh and N. Ray Chaudhuri, *Thermochim. Acta*, 1995, **268**, 153.

19 C. Pariya, M. M. Bhadbhade, A. Ghosh, B. Narayanan and N. Ray Chaudhuri, *J. Chem. Soc., Dalton Trans.*, submitted.

20 (*a*) C. Pariya, A. Ghosh, S. Ganguli and N. Ray Chaudhuri, *Thermochim. Acta*, 1994, **242**, 195; (*b*) Complexes with a cadmium : ligand ratio of 1 : 2 are characterized and reported in ref. 20(*a*). Based on previous experience and the presence of ligated water molecule in the binuclear product, an octahedral, bis-aquo structure has been formulated for **1a**.

21 C. Pariya, N. Ray Chaudhuri, S. Seth and A. Das, *Acta Crystallogr., Sect. C*, 1996, **52**, 358; C. Pariya, N. Ray Chaudhuri, A. Das and S. Seth, *Acta Chem. Scand.*, 1995, **49**, 859.

22 E. J. Gabe, Y. L. Page, J. P. Charland, F. L. Lee and P. S. White, *J. Appl. Crystallogr.*, 1989, **22**, 384.

23 G. M. Sheldrick, SHELXL-93, Program for refinement of crystal structure, University of Göttingen, 1993.

24 H. D. Flack, *Acta Crystallogr., Sect. A*, 1983, **39**, 876.

Received in Basel, Switzerland, 10th March 1997; Com. 7/01676J