

A metal dicyanamide cluster with high CO₂/N₂ selectivity



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ABSTRACT

A new microporous metal dicyanamide cluster, Co(hmt)(dca)₂ (hmt: hexamethylenetetramine, dca: dicyanamide), with accessible N-donor sites exhibits high CO₂/N₂ selectivity, 83 at 295 K and 1 bar, for a mixture with a 15:85 CO₂ to N₂ ratio. Adsorption studies show that the use of hmt and dca moieties as building blocks for solid adsorbents can enhance the CO₂:surface interactions due to N atoms available inside the pores, which is confirmed by X-ray single crystal studies.

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1. Introduction

CO₂ capture and sequestration by solid adsorbents has been of great interest in the recent years since CO₂ is believed to contribute to the increase in ocean acidity and air toxicity [1–3]. Studies show that CO₂ adsorption is governed by a combination of structural parameters such as surface area, pore volume, adsorption enthalpy, and functional groups inside the pores, e.g. active metal sites and Lewis basic groups [4–8]. Of these, introduction of accessible nitrogen atoms inside the pores has been found to be one of the most effective methods to improve CO₂/N₂ selectivity given the Lewis acid characteristic of CO₂ molecule. The promising results obtained with this approach have led research groups to focus on exploring new coordination compounds with convenient bridging groups that contain accessible nitrogen atoms [9–12].

Dicyanamide anion (dca), N(CN)₂⁻, is a versatile ligand particularly for incorporating divalent transition metal ions into various 3D lattices [13–16]. One of the common strategies in metal dicyanamide chemistry involves employing a second bridging ligand, generally a N-donor ligand, to obtain compounds with interesting magnetic and electronic properties [12,17]. These materials hold great potential also as efficient solid adsorbents that could selectively adsorb CO₂ since almost all of the metal dicyanamide clusters reported in the literature form

extended 2D or 3D structures with porous behavior. Furthermore, the nature of their cavities, e.g. the surface area and the polar functional groups inside the pores, can be tuned by choosing convenient N-donor co-ligands.

Herein this study, a new metal dicyanamide cluster was prepared, characterized, and investigated for its CO₂ and N₂ adsorption capacities. The well-established synthetic method for the preparation of dicyanamide extended networks that involves the use of N-donor molecules as co-ligands was applied to obtain a porous cluster with accessible nitrogen donor sites. Hexamethylenetetramine (hmt) with four nitrogen donor sites has been chosen as a co-ligand to increase the number of sites with Lewis base character inside the pores.

2. Experimental section

2.1. Synthesis

The starting materials Co(NO₃)₂·6H₂O, sodium dicyanamide, and hexamethylenetetramine were purchased from Aldrich and used as received. A methanol solution of hmt and sodium dicyanamide were slowly added to a methanol solution of Co(NO₃)₂·6H₂O (1 g, 3.43 mmol) to achieve a mixture with 1:1:2 (Co:hmt:dca) stoichiometric ratio. The solution was stirred for one day and filtered. The precipitate was washed with copious amounts of distilled water and methanol. The precipitate was dried in oven at 60 °C to obtain a red powder and the yield is 27%. To obtain fine crystals of the compound a 30 mL methanol

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solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (25 mg, 0.086 mmol) was slowly layered with a 30 mL methanol solution of hmt and sodium dicyanamide mixture. Red crystals were obtained after three weeks. Elemental analysis for the compound, $\text{Co}(\text{hmt})(\text{dca})_2$, $\text{CoC}_{10}\text{H}_{12}\text{N}_{10}$: calculated C 36.26, H 3.65, N 42.29; found C 36.02, H 3.33, N 41.92. IR bands (cm^{-1}): 2979(w), 2925(w), 2333(m), 2247(sh), 2184(vs), 1236(m), 1031(m), 932(m).

2.2. Instrumentation

Single-crystal X-ray data for the compound was collected on a Rigaku MicroMax 007HF diffractometer equipped with monochromatic Mo $K\alpha$ radiation. In a typical experiment, a crystal selected for study was suspended in polybutene oil and mounted on a holder. The data sets were integrated with the Rigaku CrystalClear software package. For each compound, the data set was indexed in an orthorhombic unit cell and systematic extinctions indicated the space group to be $Pnma$. Solution and refinement of the crystal structures was carried out using the SHELX [18] suite of programs and Olex2 [19], a graphical interface. Structure solution by direct methods resolved positions of all metal atoms and most of the lighter atoms. The remaining non-hydrogen atoms were located by alternating cycles of least-squares refinements and difference Fourier maps. Hydrogen atoms were placed at calculated positions and refined. The final refinement was performed with anisotropic thermal parameters for all non-hydrogen atoms. A summary of pertinent information relating to unit cell parameters, data collection, and refinements are provided in Table S3. Selected metal–ligand bond distances are provided in Table S4. CrystalMaker program was used to display the crystal structures.

The infrared studies were performed using a Bruker Tensor 27 model, Fourier transform infrared (FT-IR) spectra were recorded in transmission mode. A Digi Tech TM DLATGS detector was used with a resolution of 4.0 cm^{-1} in the $400\text{--}4000 \text{ cm}^{-1}$ range and the

spectra were recorded by 64 scans. The thermogravimetric analysis the sample was performed with TA Instruments TGA Q500 model. Measurements were made at $10^\circ\text{C}/\text{min}$ from 30 to 500°C under N_2 . CHN elemental analysis was performed with Thermo Scientific Flash 2000 model. Gas adsorption measurements were performed using a Micromeritics Tristar 3000 surface area and pore size analyzer.

3. Results and discussion

3.1. Synthesis

The use of a N-donor co-ligand (L) in the synthesis of metal dicyanamide clusters have successfully been employed previously to obtain metal dicyanamide clusters with the formula; $\text{ML}(\text{dca})_2$ [14]. The synthesis general involves the reaction of a divalent metal ion with a mixture of dca and desired N-donor ligand in polar solvents such as water, methanol, or ethanol. A similar synthetic method has been applied in this study.

Metal dicyanamide clusters, $[\text{Cd}(\text{hmt})(\text{dca})_2]$ and $\text{M}(\text{dca})_2(\text{H}_2\text{O})_n \cdot \text{hmt}_n$ ($\text{M} = \text{Co}$ and Mn), incorporating hmt as a co-ligand have already been reported [20,21]. These clusters referenced above are, however, not convenient materials for gas adsorption studies since the main drawback of cadmium cluster is its high molecular weight and that of cobalt cluster is the water molecules bound to metal ions in the structure, which could lead to the collapse of the network under vacuum. Therefore, a new metal dicyanamide with hmt ligand has been targeted in this study by changing the solvent used in the synthesis.

3.2. Structural characterization

The X-ray structural analysis of the complex clearly indicates a 3D coordination network where Co^{II} sites are connected to each other with hmt and dicyanamide bridging ligands. Each Co^{II} center

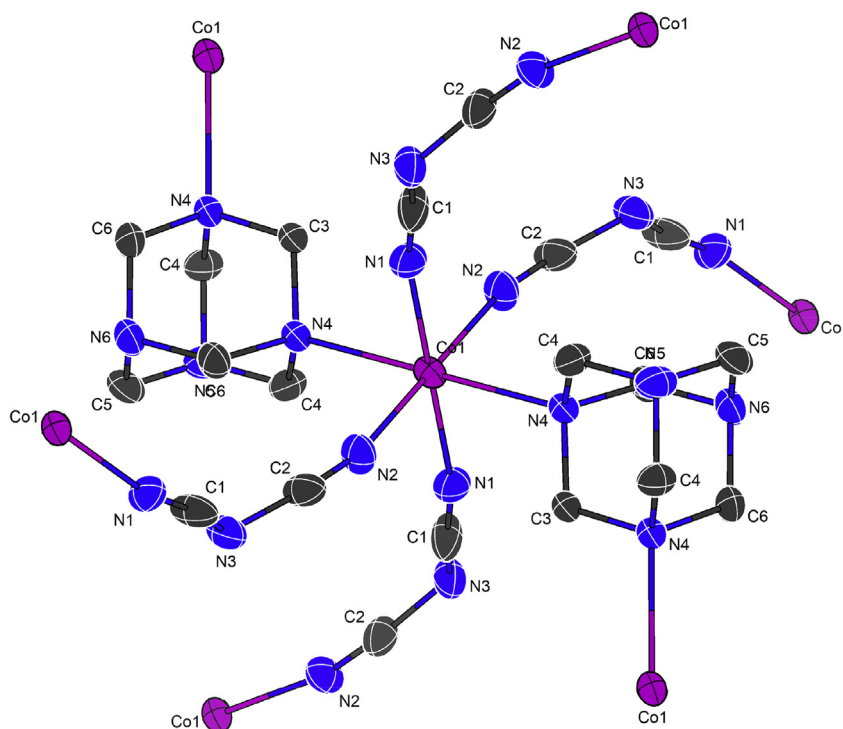


Fig. 1. Coordination sphere of Cobalt center and binding modes of bridging ligands (Hydrogen atoms are omitted for the sake of simplicity).

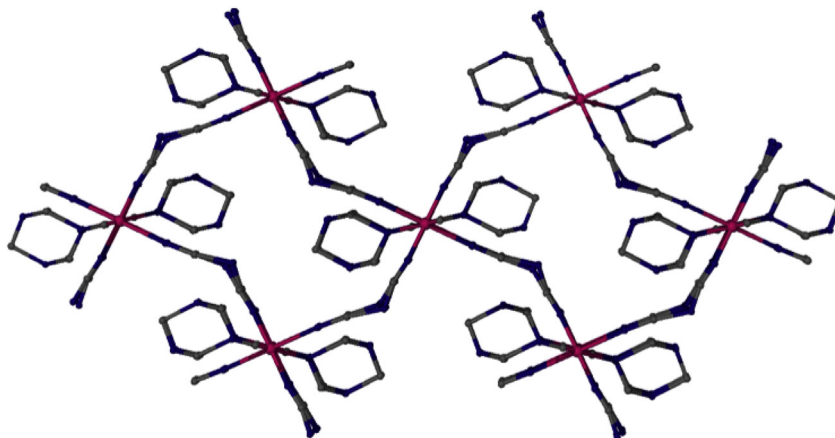


Fig. 2. 2D array of Co(dca)_2 fragments connected with hmt groups. (Hydrogen atoms are omitted for the sake of simplicity).

is surrounded by six nitrogen atoms, four of which belongs to nitrile group of dicyanamide anion while the remaining two nitrogen atoms belong to hmt groups, resulting in a distorted octahedral geometry (Fig. 1). The metal ion is located on an inversion center. Dicyanamide ligands that adopt a $\mu_{1,5}$ -dca coordination mode use their terminal nitrogen atoms to bind to metal centers. Each dicyanamide group is connected to two metal centers forming a Co_4dca_4 unit with a distorted square geometry (Fig. 2). These units form a 2D layer with the formula Co(dca)_2 . These 2D networks are then connected to each other with hmt co-ligands. Thus, the 3D structure could be best described by 2D arrays of metal-dicyanamide networks that are connected with hmt groups. It should also be noted that hmt group uses only two of its nitrogen atoms for binding to cobalt ions, leaving two free nitrogen atoms per hmt group (see Fig. 3).

Table S4 reports a selection of coordination bond lengths and angles. The distances and bond angles are in good accordance with those previously reported for metal dicyanamide and metal hexamethylenetetramine clusters [17,20].

The infrared spectrum of the compound contains three absorptions in the $\nu(\text{C}\equiv\text{N})$ region, 2184, 2247, and 2333 cm^{-1} , in addition to a stretch at 932 cm^{-1} , which are attributed to the asymmetric and symmetric cyanide stretches of dicyanamide bridging ligand. The compound also shows two strong bands at 1031 and 1236 cm^{-1} and several weak bands in the range 2900–3000 cm^{-1} , which can be assigned to the C–N and aliphatic $\nu(\text{CH})$ stretching vibrations of hmt group, respectively. Moreover, elemental analysis performed on powder materials show that powder samples used in adsorption studies and single crystals studied with X-ray single crystal technique are identical (see Fig. 4).

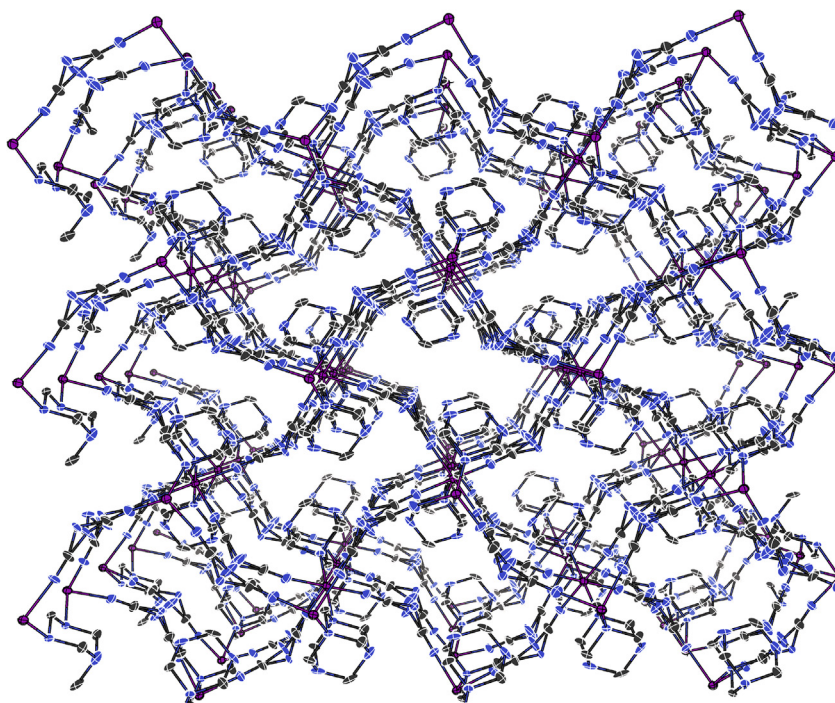


Fig. 3. Packing diagram the crystal structure. (Hydrogen atoms and solvent molecules are omitted for the sake of simplicity).

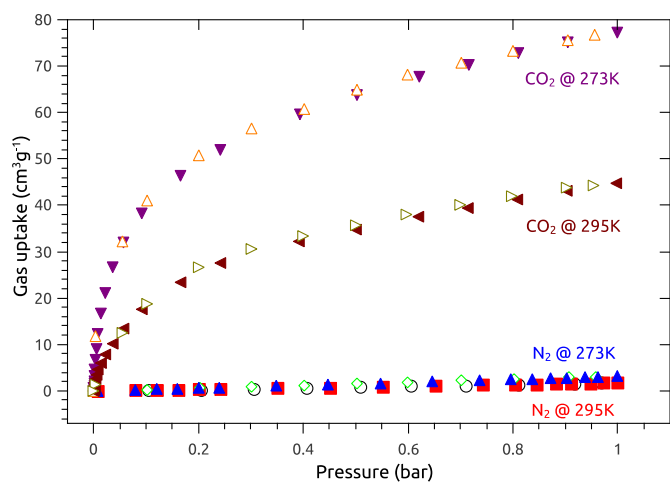


Fig. 4. Gas adsorption/desorption isotherms for CO₂ and N₂ at 273 K and 295 K. Solid symbols indicate gas adsorption and open symbols indicate gas desorption.

3.3. Gas adsorption studies

The CO₂ and N₂ adsorptions of Co(hmt)(dca)₂ were measured up to 1 bar at 273 and 295 K. The isotherms are found to be completely reversible with maximum CO₂ loadings of 77.3 cm³ g⁻¹ and 44.8 cm³ g⁻¹ at 1 bar for the temperatures of 273 K and 295 K, respectively. The CO₂ isotherms were fitted to a dual site Langmuir model (Figs. S3 and S4) and N₂ isotherms were fitted to a single site Langmuir model (Figs. S5 and S6) to calculate the selectivity and heat of adsorption values. A single-site Langmuir type model was not good enough for fitting the CO₂ adsorption data, therefore a dual-site model, which indicates two available binding sites for the CO₂ molecule [22], was used. The parameters obtained from these fittings are reported in Tables S1 and S2 in the supporting information. The heats of adsorption values were calculated using the Clausius–Clapeyron equation (see Eq. (4) in the supporting information). It can be seen from Fig. 5 that the heat of adsorption for the CO₂ adsorption increases from about 35 kJ mol⁻¹ at low loadings and reaches to a plateau of 58 kJ mol⁻¹ after 0.9 mmol g⁻¹ loading. This could be due to two different available binding sites, N-donor

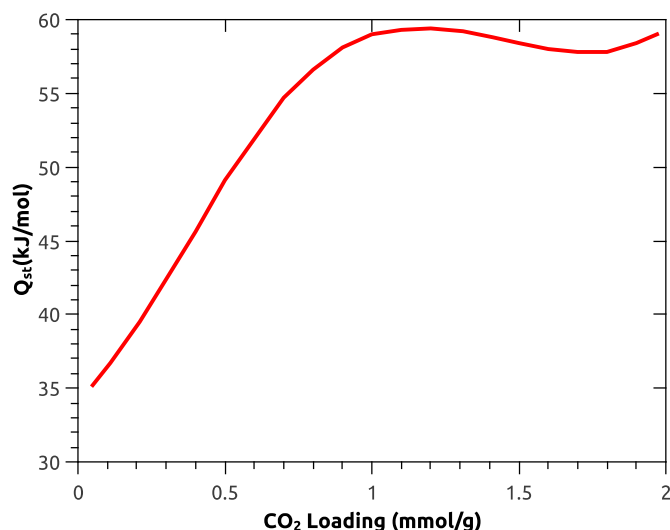


Fig. 5. Change in Q_{st} with CO₂ loading, calculated using dual-site Langmuir isotherms.

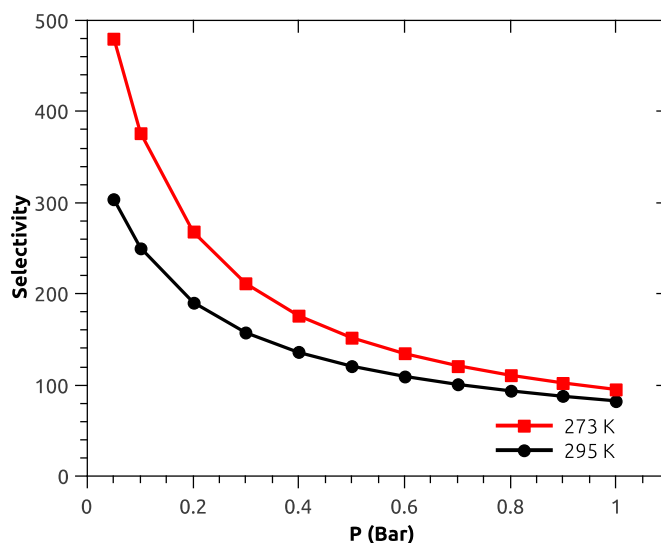


Fig. 6. Change in the CO₂ over N₂ selectivity (for a mixture of 15:85) with pressure.

atoms available at dca and hmt groups, which is expected since a dual-site Langmuir model was needed for the CO₂ adsorption isotherm fitting. The heat of adsorption for the N₂ adsorption, however, does not change appreciably with the N₂ loading and has a value of 17.7 kJ mol⁻¹. For the binary mixtures, the CO₂/N₂ selectivities were calculated using both the ratio of the initial slopes and the selectivity factor equation (see Eq. (3) in the supporting information) where loadings were obtained from the pure single component isotherms. A mixture with a 15:85 CO₂ to N₂ mole ratio was used for these calculations. The change in the selectivity with respect to the pressure is shown in Fig. 6. The CO₂/N₂ selectivity is estimated to be 95 and 83 at 273 K and 295 K, respectively, for a 15:85 CO₂/N₂ gas mixture at 1 bar. It is also observed that CO₂/N₂ selectivity decreases as the pressure of gas mixture increases. The selectivity data calculated using the Henry's law ratios (ratio of the initial slopes) from the low loading region of the single adsorption isotherms are 603 and 473 (Fig. S7). The high CO₂/N₂ selectivity can mainly be attributed to the higher adsorption enthalpy of the CO₂ (stronger interaction due to a larger quadrupole). Kinetic diameters of CO₂ and N₂ are 3.3 and 3.6 Å, respectively. Two of the pore openings for the crystal reported are around 3.8 Å, which is closer to N₂ kinetic diameter. This could limit the diffusion of N₂ into the pores and hence cause a molecular sieving effect that can contribute to the high selectivity [23,24]. Furthermore, BET surface area of the cluster, 242 m²/g, is measured by CO₂ sorption measurements at 273 K since nitrogen sorption studies at 77K failed, which is a unique phenomenon previously observed with some of the clusters studied in this field [4,25].

4. Conclusion

A new metal dicyanamide cluster, Co(hmt)(dca)₂, was successfully prepared and detailed structural characterization was performed by X-ray single crystallography. The structure contains octahedral Co^{II} sites that are connected to each other with dca and hmt bridging ligands. Each dca group uses its terminal nitrogen atoms while each hmt group uses two of its N-atoms for binding to cobalt center, leaving one and two uncoordinated N atoms in dca and hmt groups, respectively. High CO₂/N₂ selectivity and high heat of adsorption value could be attributed to the polarized environment of the pores due to the presence of aforementioned accessible

N-donor atoms. This study shows that hmt and dca moieties can be used as building blocks for MOFs and this can enhance the CO₂/N₂ selectivity of the solid adsorbents via available N atoms. Given the vast chemistry of metal dicyanamide clusters other metal dicyanamide clusters that have polar functional groups will be investigated and introduced to this field.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.micromeso.2016.03.035>.

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