

Unusual Six- and Eight-coordinated Cadmium(II) Malonate Complex: Relevance to ^{113}Cd NMR Probe of Metal Binding Sites on Metalloproteins

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The ^{113}Cd NMR spectrum of polymeric tetraaquobis(malonato)dicadmium(II) **1** is characterized by two resonances and its crystal structure shows two cadmium sites in distinct chemical environments; the six- and eight-coordinate sites formed by oxygen donors are correlated with chemical shifts at δ 18 and -107 , respectively.

^{113}Cd NMR spectroscopy has been widely used as a probe of the metal ion binding sites in many biological systems, such as metallothionein¹ and metalloenzymes.² This is because the ^{113}Cd chemical shift is highly sensitive to the types of donor atoms, coordination number and geometry. One interesting example is the ^{113}Cd chemical shift data of the S₂ site of concanavalin A³ and of the EF site of parvalbumin^{4,5} made up of oxygen donor atoms that have been observed at *ca.* δ -100 relative to 0.1 mol dm⁻³ Cd(ClO₄)₂ standard. The studies of model compounds in the identification of the nature of such biological sites have been conducted by Amma and coworkers.^{6,7} However, no examples of compounds formed with oxygen donors that give chemical shift values near δ -100 have been reported so far, except for a signal at δ -115 observed for cadmium nitrate⁸ which is not clearly involved in the Cd coordination sphere of substituted metalloproteins. As a part of further attempts to expand the ^{113}Cd chemical shift data of well defined model compounds which show chemical shift values in the biological range⁹ of δ -85 to -130 , a new type of cadmium(II) malonate compound possessing two chemically distinct cadmium sites has been synthesized. Reported herein are the results showing a correlation between ^{113}Cd chemical shift data and molecular structure.

The preparation of tetraaquobis(malonato)dicadmium(II) **1** was carried out by dissolving 4.19 g (0.01 mol) of Cd(ClO₄)₂·6H₂O (Alfa) in a 250 ml aqueous solution containing 3.32 g (0.02 mol) of disodium malonate monohydrate (Aldrich). The pH of the solution was adjusted to 6, and it was left for one week. Transparent crystals formed, which were filtered, washed with doubly deionized water, and dried.

The molecular structure† of the repeating unit in **1** is shown in Fig. 1. The crystal structure of **1** is quite different from that of cadmium(II) malonate monohydrate which only contains seven-coordinate cadmium sites.¹⁰ This crystal structure contains three cadmium atoms which are crystallographically distinct, but only two cadmium atoms are chemically and magnetically distinct. Atom Cd(1) is eight-coordinate by formation of bonds with two water molecules [O(9) and O(10)], two carboxy oxygen atoms [O(1) and O(8)] and two four-membered chelated carboxy groups which also bridge to atoms Cd(2) and Cd(3), which lie on inversion centres. The geometry around Cd(1) may be described as distorted dodecahedral. Two of the coordinated oxygen atoms [O(4) and O(6)] are further from Cd(1) than the other six oxygens. This is expected for the carboxylate groups that are both chelating and bridging: two distinct Cd–O distances are found in cadmium(II) maleate dihydrate (2.255 and 2.843 Å) and cadmium(II) calcium(II) acetate hexahydrate (2.289 and 2.677 Å) with carboxylates acting as chelating ligands.^{8,11} The atoms Cd(2) and Cd(3) have the same chemical and magnetic environment and are six-coordinate through two water molecules and four carboxy oxygen atoms: six-membered chelate rings are formed with the cadmium atom, which shows octahedral geometry. The malonate ligands link the cadmium atoms such that a layered crystal structure is formed.

The solid state ^{113}Cd NMR spectrum was obtained from *ca.* 0.5 g of the same crystalline sample on the Bruker AM 300 NMR spectrometer operating at 66.576 MHz using CP-MAS techniques. The contact time was 4 ms, the delay time was 2 s, and the rotor speed was set at 3.5 kHz. Chemical shifts are quoted relative to 0.1 mol dm⁻³ Cd(ClO₄)₂ aqueous (D₂O) solution as the reference with positive chemical shifts downfield. The spectrum of **1** thus obtained is shown in Fig. 2. The spectrum shows two signals at δ 18 and -107 . The coordination number of cadmium in cadmium–oxo compounds is six, seven or eight, while the isotropic chemical shifts span the range δ 140 to -115 .^{8,11} From these observations, a pattern has emerged showing that six-coordinate Cd²⁺ has a ^{113}Cd chemical shift ranging from δ 140 to -70 , seven-coordinate cadmium spans the range δ 0 to -70 , and eight-coordinate cadmium a range δ 0 to -115 . Based on such findings, the chemical shift at δ 18 was assigned to the six-coordinate Cd(2) and Cd(3) atoms which are in magnetically equivalent environments, and the peak at δ -107 to the eight-coordinate Cd(1) atom.

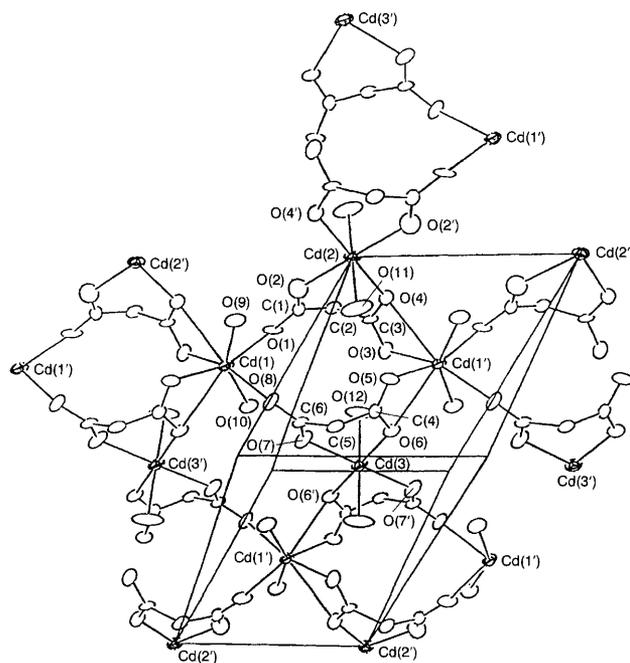


Fig. 1 Molecular structure of **1**. The unit cell outline is drawn in to show the repeating unit. The two cadmium atoms, Cd(2) and Cd(3) lie on inversion centres and atoms labelled with primes indicate symmetrically related ones. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Cd(1)–O(1) 2.323(4), Cd(1)–O(3) 2.307(4), Cd(1)–O(4) 2.775(5), Cd(1)–O(5) 2.314(4), Cd(1)–O(6) 2.775(5), Cd(1)–O(8) 2.310(4), Cd(1)–O(9) 2.375(4), Cd(1)–O(10) 2.375(4), Cd(2)–O(2) 2.296(4), Cd(2)–O(4) 2.225(4), Cd(2)–O(11) 2.277(5) Å; O(1)–Cd(1)–O(8) 91.3(2), O(9)–Cd(1)–O(10) 151.5(2), O(3)–Cd(1)–O(4) 49.8(2), O(5)–Cd(1)–O(6) 49.9(2), O(2)–Cd(2)–O(4) 85.0(1)°.

Three eight-coordinate cadmium–oxo compounds with quite different chemical shifts are reported in the literature: cadmium(II) nitrate tetrahydrate (**2**: δ -115), cadmium(II) calcium(II) acetate hexahydrate (**3**: -29) and cadmium(II) maleate dihydrate (**4**: -22).^{8,11} The eight-coordinated cadmiums of these compounds also have distorted dodecahedral structures. Compounds **3** and **4** are coordinated only by carboxy oxygens, while compound **2** has four long-bonded oxygens from bidentate nitrates and four from water molecules. The unusual upfield shift of **2** among eight-coordinate cadmium species is discussed in terms of the shielding influence of weak ligands (e.g. nitrate and sulfate) with weak bonding interactions.⁹ The eight-coordinate cadmium in **1** has two coordinated water molecules and also appeared more shielded than those of **3** and **4**. The bond length, local site symmetry and type of ligands all make contributions to chemical shift values¹¹ and the presence of coordinated water molecules may cause a shielding influence on eight-coordinate cadmium.

In summary, a new eight-coordinate cadmium site in **1** constitutes the first such example with biologically relevant ligands and the chemical shift value (δ -107) of this eight-coordinate cadmium shows an isotropic shift that lies within the

range observed for the metalloproteins concanavalin A³ and parvalbumin.^{4,5}

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Footnote

† *Crystal data*: polymeric tetraaquobis(malonato)dicalcium(II), $\text{Cd}_2(\text{C}_3\text{H}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$, $M = 500.96$, triclinic, space group $P\bar{1}$, $a = 7.276(2)$, $b = 8.180(3)$, $c = 12.483(2)$ Å, $\alpha = 76.14(2)$, $\beta = 73.13(2)$, $\gamma = 63.65(2)^\circ$, $U = 631.8$ Å³, $Z = 2$, $D_c = 2.633$ g cm⁻³, $R_1(wR_2) = 0.0321$ (0.0854) for 1953 observed data [$F_o > 4.0\sigma(F_o)$]. The diffraction data of a transparent crystal were collected on an Enraf-Nonius CAD4TSB diffractometer with graphite-monochromated Mo-K α radiation at 296 K. All data were collected with the ω - 2θ scan mode and corrected for L_p effects. No absorption correction was applied. The structure of this compound was solved by direct methods (SHELXS 86) and full-matrix least-squares procedures (SHELXL 93) on an IBM RISC/6000 Workstation. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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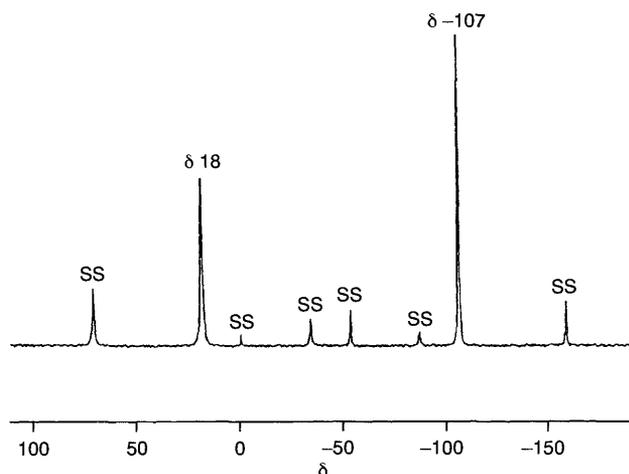


Fig. 2 ¹¹³Cd CP-MAS NMR spectrum of **1**. Peaks labelled as SS are spinning sidebands.