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Cd–Cd Coupling in the ^{113}Cd NMR Spectra (including 2-dimensional COSY) of Molecular Polycadmium Thiolate Aggregates

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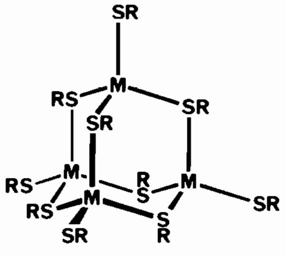
We report the measurement of Cd–Cd ^2J coupling in the natural abundance* ^{113}Cd NMR spectra of polycadmium thiolate/chalcogenide aggregates of known crystal structure, and the applications of ^{113}Cd NMR to investigation of the reactions of these aggregates. These results establish characteristics of Cd–Cd coupling, previously observed in ^{113}Cd enriched metallothioneins [1] and in oligomers of unknown structure with a bis-cysteinyl derivative of EDTA [2].

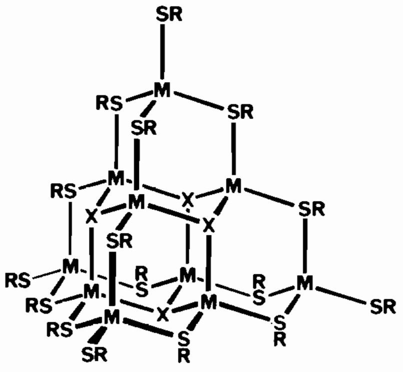
The ^{113}Cd spectrum (obtained on a Bruker CXP-300 spectrometer at 66.6 MHz, external reference 0.2 M aqueous $Cd(NO_3)_2$) of the adamantanoid cage $[Cd_4(SPh)_{10}]^{2-}(Me_4N^+)$, **1** [3, 4] in MeCN contains a single resonance at 578 ppm (300 K), and shows the doublet satellites each of relative intensity *ca.* 20% due to ^{113}Cd–S–^{111}Cd isotope coupling with $^2J(^{113}\text{Cd–S–}^{111}\text{Cd})$ = 44 Hz. The Cd_4S_{10} core of **1** has virtual T_d symmetry, and consequently the calculated intensities of the septuplet for **1** are 0.04, 1.55, 21.4, 100, 21.4, 1.55, 0.04. By partial ^{113}Cd enrichment of **1** and measurement of ^{111}Cd, Dean has observed all of the expected satellite peaks [5]. This Cd–Cd coupling is observed even though there is rapid (NMR time scale) exchange of thiolate ligands in **1** [6] and confirms that the exchange process is an intramolecular exchange of bridging and terminal thiolate ligands.



1

M = Cd

* ^{113}Cd, I = ½, 12.3%, ^{111}Cd, I = ½, 12.8%.



2

M = Cd, X = S, Se

The tetra-adamantanoid aggregate $[S_4Cd_{10}(SPh)_{16}]^{4-}$ **2**, also with virtual T_d symmetry for the $Cd_{10}S_{20}$ core, contains six inner Cd atoms (Cd_i) arrayed as an octahedron, four outer Cd atoms (Cd_o) arrayed as a tetrahedron, four triply-bridging sulfide ions, twelve doubly-bridging thiolate ligands (S_{br}), and four terminal thiolate ligands, with structural equivalence occurring in each set [4]. The ^{113}Cd spectrum of **2** (DMF, 300 K, see Fig. 1) has the Cd_i resonance at 668 ppm and the Cd_o resonance at 585 ppm. The Cd_i signal is attended by the doublet and triplet wings of the 0.0026, 0.147, 3.02, 27.9, 100, 27.9, 3.02, 0.147, 0.0026 nonaplet calcu-

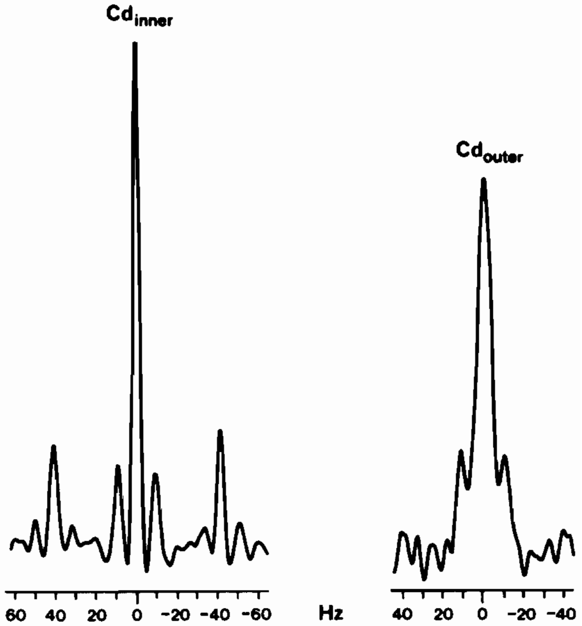


Fig. 1. The $^{113}Cd_i$ (668 ppm) and $^{113}Cd_o$ (585 ppm) resonances of $[S_4Cd_{10}(SPh)_{16}]^{4-}$ **2**, in DMF solution, 300 K, reference 0.2 M aqueous $Cd(NO_3)_2$. The weak triplet satellites at ±82 Hz to Cd_i are revealed with different processing of the FID.

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TABLE I. ^{113}Cd Resonances Observed[a] in Reactions of $[S_4Cd_{10}(SPh)_{16}]^{4-}$ with Cd^{2+} in DMF.

Line[b]	Comments	
670	doublet satellites, J = 73 Hz	intensity correlated
669		with peak 584
668	$[S_4Cd_{10}(SPh)_{16}]^{4-}$, doublet, triplet satellites, J = 82 Hz	
	doublet satellites, J = 18 Hz	
658	temporal intermediate at 300 K	
638	in solutions heated to 350 K:	intensity correlated with 588
628	temporal intermediate at 300 K	
618	doublet satellites, J = 104 Hz:	doublet satellites, J = 35 Hz
613	temporal intermediate at 300 K	
608	doublet satellites, J = 42 Hz: coupled (COSY, and by intensity correlation with 567)	
599	at Q[c] > 0.6, low temperature	
590	doublet satellites, J = 42 Hz: dominant when Q > 1.8	
588	(see 638)	
585	$[S_4Cd_{10}(SPh)_{16}]^{4-}$, doublet satellites, J = 18 Hz	
584	(see 670, 669)	
580	weak	often broad and not resolved, intense in solutions
578		heated to 350 K, Q < 0.8
567	doublet, triplet satellites, J = 43 Hz: (see 608)	
563	weak	
557	doublet satellites, J = 45 Hz	
539	weak	
501	broad, for t < 100 min	

[a]Natural abundance ^{113}Cd, 66.547 MHz. [b]Resonances are labelled with the chemical shift (ppm, referenced to 0.2 M aqueous $Cd(NO_3)_2$) at 300 K. Temperature dependences of chemical shifts are substantial (up to 0.2 ppm K^{-1}) and variable. [c]Q is the molar ratio Cd^{2+}: $[S_4Cd_{10}(SPh)_{16}]^{4-}$.

lated for $^{113}Cd_i$–$^{111}Cd_i$ isotope coupling at natural abundance, with $^2J(^{113}Cd_i–S–^{111}Cd_i)$ = 82 Hz. The Cd_o–S–Cd_i coupling through doubly-bridging thiolate is 18 Hz**, and is manifest as its doublet components on the Cd_i and Cd_o resonances. A 2-D COSY spectrum# of 2 clearly shows the cross peak: this is the first report of a Cd–Cd COSY measurement. In the isostructural selenide homologue, $[Se_4Cd_{10}(SPh)_{16}]^{4-}$, 2, X = Se, Cd_i is at 592 ppm, Cd_o at 576 ppm, $^2J(^{113}Cd_i–Se–^{111}Cd_o)$ = 101 Hz, and $^1J(^{113}Cd_i–^{77}Se)$ = 151 Hz.

The ^{13}C spectrum of 2 (260–300 K) reveals the coupling to Cd of C_1 and $C_{2,6}$ in both the bridging and terminal thiolate ligands: bridging, $^2J(^{13}C–S–^{111,113}Cd)$ = 9 Hz, $^3J(^{13}C–C–S–^{111,113}Cd)$ = 9 Hz: terminal, $^2J(^{13}C–S–^{111,113}Cd)$ = 16 Hz, $^3J(^{13}C–C–S–^{111,113}Cd)$ = 20 Hz. Coalescence of the terminal and bridging thiolate resonances occurs at *ca.* 340 K, due to intramolecular exchange. The exchange in 2 is much slower than that in 1, but probably follows the same mechanism [6].

Cd–Cd coupling of the type reported here provides unequivocal reference data, and enhances the prospects of determining solution structure for polycadmium species (although enrichment may be required to reveal complete satellite patterns in high symmetry aggregates). We have deployed ^{113}Cd NMR to investigate the reactions of 2 with electrophiles, particularly with $Cd(NO_3)_2$ in DMF solution. Rich ^{113}Cd spectra are obtained, revealing multiple products and reaction pathways, with the following principal characteristics:

(i) 2 is sensitive to small proportions of Cd^{2+}, with maximum product concentrations occurring when the Cd^{2+}: $[S_4Cd_{10}(SPh)_{16}]^{4-}$ molar ratio, Q, is in the range 0.2 to 1.5.

(ii) There are at least two stages of reaction, with the first stage complete within 5 min at 273 K, while the second stage has a half-life of many hrs at 315 K (dependent on concentrations of both Cd^{2+} and 2 ($3–7 \times 10^{-2}$ M Cd_{10})).

(iii) Solutions heated to 350 K give different products.

(iv) 19 new resonances are observed, and are listed in Table I together with a summary of the observed

**$^2J(^{113}Cd–^{111}Cd)$ and $^2J(^{113}Cd–^{113}Cd)$, which differ by 4%, are not resolvable.

#The standard COSY pulse sequence [7] for N type peaks was used with phase cycling to remove unwanted axial and P type absorptions. The sweep width in both directions was ±3500 Hz. The two-dimensional array was 2 K × 1 K obtained by zero-filling the 128 × 1 K experimental spectra.

Cd–Cd coupling satellites, and the groups of resonances for which intensity changes are correlated.

The chemical shift range for the new resonances indicates predominant (if not exclusive) coordination of Cd by S donors, and the coupling observed confirms the expectation from the stoichiometry that S-bridged polycadmium aggregates are present. At least three new aggregates are formed, and we are attempting to determine the compositions and structures of these species by use of enriched ^{113}Cd to allow full observation of the coupling patterns, and by crystallization and diffraction analysis.

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