An Approximately Tetrahedral CdS₄ Moiety. The Structure of Tetrakis(*N*,*N'*-dimethylthiourea-*S*)cadmium(II) Nitrate, C₁₂H₃₂CdN₈S₄.2NO₃, and its ¹¹³Cd CP/MAS NMR

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Abstract. $M_r = 653 \cdot 1$, orthorhombic, $Pc2_1n$, $a = 7 \cdot 378$ (2), $b = 10 \cdot 653$ (4), $c = 35 \cdot 16$ (1) Å, $V = 2763$ (3) Å³, $Z = 4$, $D_m = 1 \cdot 55$ (2), $D_x = 1 \cdot 570$ g cm⁻³, Mo $K\alpha$, $\lambda = 0 \cdot 71073$ Å, $\mu = 11 \cdot 23$ cm⁻¹, $F(000) = 1328$, $T \sim 291$ K, $R = 0 \cdot 058$, $R_w = 0 \cdot 074$ for 2266 observations. Compound synthesized by authors. The structure consists of isolated ionic species of [tetrakis(*N*,*N'*-dimethylthiourea-*S*)Cd]²⁺ and 2NO₃⁻. The Cd has a very distorted tetrahedral CdS₄ environment with Cd–S distances 2·496 (6) to 2·56 (1) Å and S–Cd–S angles of 100·2 (3) to 118·1 (3)°. The distances and angles within the planar *N*,*N'*-dimethylthiourea groups are normal. There exists some disorder in one of the nitrate groups and some of the methyl groups. The solid-state CP/MAS ¹¹³Cd NMR consists of nine peaks between +240 and +610 p.p.m. [deshielded from the aqueous Cd(ClO₄)₂ standard]. The limitations of solid-state ¹¹³Cd NMR in proteins and enzymes are discussed.

Introduction. ¹¹³Cd NMR shows considerable promise as a probe of Zn²⁺, Ca²⁺ sites of proteins and enzymes (Rodesiler, Griffith, Ellis & Amma, 1980; Rodesiler & Amma, 1982). The advent of cross-polarization magic-angle spinning (CP/MAS) ¹¹³Cd NMR observations in the solid state (Cheung, Worthington, Murphy & Gerstein, 1980; Mennitt, Shatlock, Bartuska & Maciel, 1981; Murphy & Gerstein, 1981; Rodesiler & Amma 1982; Yannoni, 1982; Lyerla, Yannoni & Fyfe, 1982) makes it attractive to consider the NMR of this nucleus as a tool in studying solid proteins whether the samples are as powders or single crystals. We have been actively synthesizing models for structural and enzymatic Cd²⁺ sites in which Cd²⁺ replaces Ca²⁺ or Zn²⁺ and determining their crystal structures, and measuring solution and CP/MAS solid-state ¹¹³Cd NMR. As part of this investigation, we have synthesized a number of four-coordinated sulfur-bound Cd models (CdS₄). We wish to report on the structure of one of those herein

and point out some of the difficulties that are involved in model compounds and their implications on the limitations of solid-state ¹¹³Cd NMR of proteins and enzymes. A detailed discussion of the correlation of crystal structures, solution and solid-state ¹¹³Cd NMR of a number of tetrahedral CdX_4 systems will be published elsewhere.

Table 1. *Positional parameters and their e.s.d.'s*

$$B_{eq} = \tfrac{8}{3}\pi^2 \sum_i \sum_j U_{ij}\, a_i^*\, a_j^*\, \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	B_{eq}(Å²)	Pop†
C(231)	0·3000‡	0·1037	0·2041	5·95	0·85
C(232)	0·4802	0·1566	0·1650	8·67	0·15
N(10.1)	0·3018	0·7476	0·2477	6·51	0·50
N(10.2)	0·3447	0·7456	0·2439	4·26	0·50
O(4)	0·2791	0·6463	0·2564	7·94	
O(5)	0·4599	0·7905	0·2622	11·82	
O(61)	0·1982	0·7983	0·2304	8·37	0·50
O(62)	0·2727	0·7712	0·2131	11·12	0·50
Cd	0·0320 (1)	0·2504§	0·09041 (2)	3·52 (6)	
S(1)	0·2591 (5)	0·4030 (4)	0·1204 (1)	3·8 (1)	
S(2)	0·2194 (5)	0·0477 (4)	0·0914 (1)	4·5 (1)	
S(3)	0·0230 (5)	0·2941 (4)	0·02008 (9)	4·2 (2)	
S(4)	−0·2647 (5)	0·2184 (4)	0·1231 (1)	4·5 (2)	
N(11)	0·270 (2)	0·481 (1)	0·1918 (4)	4·3 (6)	
N(12)	−0·002 (1)	0·510 (1)	0·1608 (4)	3·9 (5)	
N(21)	0·282 (2)	0·092 (1)	0·1527 (5)	5·2 (7)	
N(22)	0·275 (2)	0·115 (1)	0·1627 (4)	4·5 (6)	
N(31)	0·320 (1)	0·349 (1)	0·0284 (4)	4·3 (7)	
N(32)	−0·254 (2)	0·215 (1)	0·0206 (3)	3·9 (5)	
N(41)	0·261 (2)	0·028 (1)	0·1071 (4)	4·2 (6)	
N(42)	0·222 (2)	0·029 (1)	0·1692 (4)	4·4 (7)	
C(11)	0·167 (2)	0·469 (1)	0·1599 (4)	3·6 (6)	
C(12)	0·455 (2)	0·448 (2)	0·1958 (7)	7·(1)	
C(13)	−0·089 (3)	0·568 (2)	0·1937 (6)	6·3 (7)	
C(21)	0·260 (2)	0·021 (1)	0·1390 (4)	2·9 (5)	
C(22)	0·261 (3)	0·209 (2)	0·1288 (6)	6·(1)	
C(31)	−0·205 (2)	0·284 (1)	0·0093 (4)	3·1 (6)	
C(32)	−0·523 (2)	0·336 (3)	0·0229 (6)	8·(1)	
C(33)	0·127 (4)	0·138 (2)	0·0429 (6)	7·(1)	
C(41)	−0·246 (2)	0·059 (1)	0·1345 (4)	3·3 (6)	
C(42)	−0·281 (3)	−0·007 (2)	0·0661 (5)	5·6 (7)	
C(43)	0·210 (3)	0·100 (2)	0·1849 (5)	5·6 (7)	
N(9)	0·199 (2)	0·117 (1)	0·4102 (4)	4·2 (7)	
O(1)	0·267 (2)	0·010 (1)	0·4083 (4)	4·7 (6)	
O(2)	0·235 (2)	0·194 (1)	0·3854 (4)	6·4 (7)	
O(3)	0·100 (2)	0·142 (1)	0·4382 (4)	6·5 (7)	

† Population parameters for disordered atoms: positional parameters not refined.

‡ Values with no e.s.d.'s are for invariant positions which were not refined.

§ Cd y coordinate defines origin and is not variable.

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Table 2. *Bond lengths (Å) and angles (°) and least-squares planes data*

Cd–S(1)	2·56(1)	C(21)–N(22)	1·31(3)	N(31)–C(32)	1·52(2)
Cd–S(2)	2·56(1)	C(31)–N(31)	1·28(2)	N(32)–C(33)	1·47(3)
Cd–S(3)	2·517(5)	C(31)–N(32)	1·34(2)	N(41)–C(42)	1·47(2)
Cd–S(4)	2·496(6)	C(41)–N(41)	1·34(3)	N(42)–C(43)	1·48(2)
S(1)–C(11)	1·70(2)	C(41)–N(42)	1·27(2)	N(10,1)–O(4)	1·13
S(2)–C(21)	1·72(2)	N(11)–C(12)	1·42(2)	N(10,1)–O(5)	1·35
S(3)–C(31)	1·73(2)	N(12)–C(13)	1·46(2)	N(10,1)–O(6,1)	1·12
S(4)–C(41)	1·75(2)	N(21)–C(22)	1·51(2)	N(10,2)–O(4)	1·24
C(11)–N(11)	1·36(2)	N(22)–C(231)	1·47	N(10,2)–O(5)	1·17
C(11)–N(12)	1·32(2)	N(22)–C(232)	1·58	N(10,2)–O(6,2)	1·24
C(21)–N(21)	1·31(2)			N(9)–O(1)	1·25(2)
				N(9)–O(2)	1·23(2)
				N(9)–O(3)	1·26(2)

S(1)–Cd–S(2)	100·2(3)	S(4)–C(41)–N(42)	119(1)
S(1)–Cd–S(3)	107·7(4)	C(11)–N(11)–C(12)	127(2)
S(1)–Cd–S(4)	118·1(3)	C(11)–N(12)–C(13)	125(1)
S(2)–Cd–S(3)	100·6(3)	C(21)–N(21)–C(22)	123(1)
S(2)–Cd–S(4)	110·6(4)	C(231)–N(22)–C(232)	82
S(3)–Cd–S(4)	117·0(2)	C(21)–N(22)–C(231)	125
Cd–S(1)–C(11)	109·7(7)	C(21)–N(22)–C(232)	109
Cd–S(2)–C(21)	104·1(7)	C(31)–N(31)–C(32)	122(1)
Cd–S(3)–C(31)	103·2(6)	C(31)–N(32)–C(33)	124(1)
Cd S(4) C(41)	100·0(7)	C(41)–N(41)–C(42)	127(1)
S(1)–C(11)–N(11)	119(1)	C(41)–N(42)–C(43)	127(1)
S(1)–C(11)–N(12)	122(1)	O(4)–N(10,1)–O(5)	110
S(2)–C(21)–N(21)	122(2)	O(4)–N(10,1)–O(6,1)	120
S(2)–C(21)–N(22)	121(2)	O(5)–N(10,1)–O(6,1)	129
S(3)–C(31)–N(31)	120(1)	O(4)–N(10,2)–O(5)	115
S(3)–C(31)–N(32)	118(1)	O(4)–N(10,2)–O(6,2)	109
S(4)–C(41)–N(41)	120(1)	O(5)–N(10,2)–O(6,2)	134
N(11)–C(11)–N(12)	120(2)	O(1)–N(9)–O(2)	119(1)
N(21)–C(21)–N(22)	118(2)	O(1)–N(9)–O(3)	118(1)
N(31)–C(31)–N(32)	123(1)	O(2)–N(9)–O(3)	122(1)
N(41)–C(41)–N(42)	120(2)		

Planes
1. S(1)–Cd–S(2)
2. S(1)–Cd–S(3)

3. S(1)–Cd–S(4)
4. S(2)–Cd–S(3)
5. S(2)–Cd–S(4)
6. S(3)–Cd–S(4)
7. S(1)–C(11)–N(11)–N(12)
8. C(11)–N(12)–C(13)
9. C(11)–N(11)–C(12)

10. S(2)–C(21)–N(21)–N(22)
11. a. C(21)–N(22)–C(231)
    b. C(21)–N(22)–C(232)
12. C(21)–N(21)–C(22)
13. S(3)–C(31)–N(31)–N(32)
14. C(31)–N(32)–C(33)
15. C(31)–N(31)–C(32)
16. S(4)–C(41)–N(41)–N(42)
17. C(41)–N(42)–C(43)
18. C(41)–N(41)–C(42)

Angles between planes

Planes	Angle (°)	Planes	Angle (°)	Planes	Angle (°)
1,6	88(1)	7,9	1(1)	13,14	5(1)
2,5	90(1)	10,11a	5	13,15	7(1)
3,4	88(1)	10,11b	89	16,17	3(1)
7,8	0(1)	10,12	3(1)	16,18	4(1)

Experimental. Preparation: 1·04 g (10 m mol) of N,N'-dimethylthiourea (K & K) and 1·54 g (5 m mol) $Cd(NO_3)_2.4H_2O$ dissolved in 150 ml H_2O with gentle heating ($\sim$ 330 K) for $\sim$ 30 min and allowed to evaporate slowly at ambient temperature, diffraction quality crystals collected after 6–8 d without washing and air dried. Crystal $\sim$0·62 × 0·22 × 0·19 mm, Enraf–Nonius ,CAD-4 interfaced to a PDP 11/60 (Enraf–Nonius, 1980), D_m by flotation in $CCl_4.CHBr_3$, $0kl$ $l = 2n + 1$, $hk0$ $h + k = 2n + 1$ absent, faces: $(\bar{1}00)$ (101) $(10\bar{1})$ (001) $(00\bar{1})$ (010) $(0\bar{1}0)$, absorption corrections made, transmission factors: max. 0·901, min. 0·670 (Frenz, 1980), graphite monochromator, $\theta = 6 \cdot 10$, $P = 0.030$ in $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (P\ I_{raw})^2]^{1/2}/Lp$, $w = 1/\sigma(F_o)^2$, $F^2 > 4\sigma(F_o^2)$, 3699 hkl, ω–2θ mode, $2\theta_{max} = 60°$, $h = 0$–10, $k = 0$–14, $l = -28$–49, 2266 reflections used, 185 unobserved with $F_{min} = 13 \cdot 0$,

variable scan speed starting at 4° min$^{-1}2\theta$, 25 general reflections in orientation matrix (checked every 24 h) used in cell-parameter measurements, 3 standard reflections every 100 reflections, decay less than 2% I, $R_{int} = 0.025$, full-matrix least squares, anisotropic, anomalous-dispersion corrections with weights based upon intensity statistics (Frenz, 1980), $\sum_i w_i[\ |F_o| - |F_c|_i]^2$ minimized, Amdahl V6 (XRAY: Stewart, 1979), f, f', f'' from *International Tables for X-ray Crystallography* (1974), largest shift 0·05 σ, average 0·01 σ, 252 variables, $R = 0.058$, $R_w = 0.074$, error of observations of unit weight = 4·12,* final difference Fourier qualitatively featureless, H atoms not located, no extinction corrections.†

Discussion. The atomic coordinates are listed in Table 1 and the distances and angles as well as least-squares planes are listed in Table 2. The structure analysis was complicated by extensive disorder in one of the nitrate ions and one of the methyl groups. The disordered nitrate group as specified by N(10,1)N(10,2) was fitted as well as possible by considering a fixed nitrate-group geometry and variable group-atom populations to fit peaks that were related by translations and/or rotations. Not all the disorder could be satisfactorily accounted for by this means, but it was decided that it was not profitable to continue with further nitrate-group disorder. Methyl group C(23) was also clearly disordered and could be fitted by two peaks with isotropic temperature factors. In addition C(32) and C(33) have large B equivalents at 8 and 7 Å^2, respectively, and large U_{ij} of $> 0 \cdot 10$ Å^2 in one direction, but difference Fourier maps with these atoms excluded did not show more than one well defined peak. These carbon atoms are probably also disordered, but a disordered description is no better than the large thermal motion as presented herein.

The structure may be described as isolated molecular ions of tetrakis(N,N'-dimethylthiourea)Cd^{II} and nitrate ions (Fig. 1) with only normal van der Waals distances between ions (Fig. 2). The environment about Cd is that of a considerably distorted tetrahedron with S—Cd—S angles ranging from 100·2 (3) to 118·1 (3)° and Cd—S distances varying from 2·496 (6) to 2·56 (1) Å. The distortion is not a simple compression of the tetrahedron to a D_{2d} geometry, but is much more irregular (Table 2, least-squares planes). However, there is very
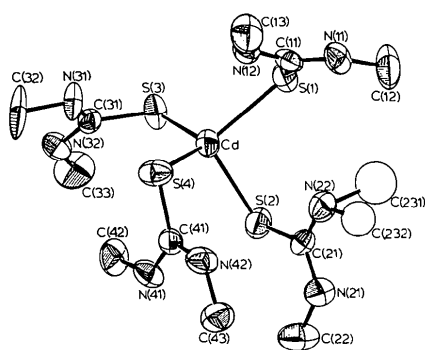
Fig. 1. An *ORTEP* (Johnson, 1970) view of the tetrakis(*N,N'*-dimethylthiourea)Cd[II] ion with notation consistent with text and tables. The ellipsoids are drawn at the 50% probability level. The disorder in the terminal methyl group attached to N(22) is indicated by the open circles representing the two possible positions. It is clear that large thermal motions or disorder are present in some of the other terminal methyl groups, but disordered models are no improvement over large thermal parameters.
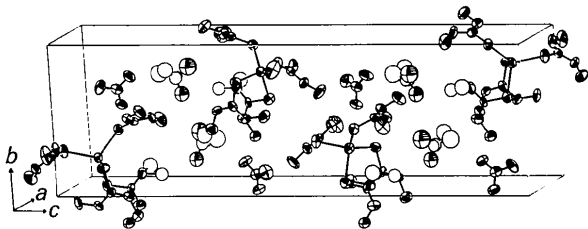

Fig. 2. An *ORTEP* (Johnson, 1970) view of the contents of the unit cell of tetrakis(*N,N'*-dimethylthiourea)Cd[II] nitrate. The origin of the unit cell is at the front left-hand corner as indicated. The disorder in the cations is discussed in the text. One of the nitrate groups is obviously normal. The other is disordered as if two oxygens of the nitrate group are normal and alternative disordered positions exist for the remaining oxygen and the nitrogen atom, *i.e.* the two normal oxygen atoms behave as the fixed end of a hinge.

little twisting of the tetrahedron as seen from the first six angles between planes 1 to 6, Table 2. The thiourea groups are planar well within experimental error and the individual distances and angles are those expected. It is somewhat surprising that the carbon atoms of the terminal methyl groups are essentially coplanar with the thiourea group, *e.g.* angle between planes 7 and 8.

The solid-state cross-polarization magic-angle spinning ^{113}Cd NMR of the present compound should be representative of CdS_4 structural sites in proteins such as that of horse liver alcohol dehydrogenase. However, the distorted geometry about Cd, *i.e.* high asymmetry, even at a sample spinning speed of 4 kHz, leads to as many as nine individual ^{113}Cd NMR peaks between

+240 and +610 p.p.m. deshielded from the $Cd(H_2O)_6(ClO_4)_2$ standard. It is very difficult to sort out this number of peaks to find the ^{113}Cd resonance at rotor speeds less than 6 kHz. Unfortunatley, no one has built a rotor that can withstand this spinning speed and at this time little more can be said of the CP/MAS solid-state ^{113}Cd of this compound. However, its implications in the observation of ^{113}Cd NMR of proteins in the solid state is of some importance. A distorted geometry of the tetrahedral structural site of a Cd^{2+} substituted for a Zn^{2+} is not an unexpected feature. Therefore, it is very likely that all one might observe in a solid protein is the weak broad envelope of what we have observed in the present compound. Considering the number of ^{113}Cd nuclei in the present compound compared to that in even a small protein in a comparable sample, which may be difficult to obtain, this may make the observation of a ^{113}Cd NMR in a solid metallo protein difficult. This limitation is above and beyond the obvious one of the integrity of the protein in a given solid sample compared to that in solution or in a single crystal.

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