Acta Cryst. (1983). C**39**, 331–333

A Tetrahedral CdS_2O_2 Stereochemistry: The Structure of (Dinitrato-*O*)bis(1,1,3,3-tetramethyl-2-thiourea-*S*)cadmium(II), $Cd(C_5H_{12}N_2S)_2(NO_3)_2$, and its ^{113}Cd NMR Spectra

By E. A. H. Griffith, N. G. Charles, P. F. Rodesiler and E. L. Amma*

Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208, *USA*

(*Received* 16 *August* 1982; *accepted* 1 *November* 1982)

Abstract. $C_{10}H_{24}CdN_6O_6S_2$, $M_r = 500{\cdot}9$, monoclinic, $P2_1/c$, $a = 12{\cdot}507$ (4), $b = 7{\cdot}270$ (4), $c = 21{\cdot}67$ (1) Å, $\beta = 95{\cdot}42$ (4)°, $V = 1961$ Å^3, $Z = 4$, $D_x = 1{\cdot}696$, $D_m = 1{\cdot}68$ (1) g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 13{\cdot}51$ cm^{-1}, $F(000) = 1016$, $T \sim 291$ K, $R = 0{\cdot}054$, $R_w = 0{\cdot}060$ for 2897 observations. Compound synthesized by authors. The structure consists of isolated ion triplets from an approximately tetrahedral environment about Cd with Cd–S distances of 2·498 (2) Å and Cd–O distances of 2·295 (4) Å. These species are separated from their neighbors by ordinary van der Waals distances. The solid-state magic-angle spinning ^{113}Cd NMR of this compound was observed at +263 p.p.m, deshielded from the aqueous $Cd(ClO_4)_2$ standard.

Introduction. ^{113}Cd NMR spectroscopy with a chemical shift range of ~ 900 p.p.m. has been shown in recent years to have considerable chemical potential as a sensitive probe of metalloproteins and metalloenzymes (Rodesiler, Griffith, Ellis & Amma, 1980; Rodesiler & Amma, 1982). The advent of solid-state magic-angle spinning (MAS) ^{113}Cd NMR spectroscopy has further broadened the scope of this nucleus as a probe (Mennitt, Shatlock, Bartuska & Maciel, 1981). With these NMR tools available, a correlation of ^{113}Cd NMR and solid-state structure is an attractive endeavor.

The four-coordinate Cd moieties containing 4S, 2S–2O, 2S–2N and 2S–N–O combinations of donor ligands to Cd^{2+} are particularly interesting as models for metal sites in various enzymes in which Cd is used as a probe of Zn^{2+} enzymatic or structural locei (Otvos & Armitage, 1979; Sadler, Bakka & Beynon, 1978; Bobsein & Myers, 1981; Jensen, Deshmukh, Jakobsen, Inners & Ellis, 1981; Linse, Gustavsson, Lindman & Drakenberg, 1981; Briggs & Armitage, 1982). The titled compound is a precursor to compounds which are models for these enzymatic sites. We have observed the ^{113}Cd MAS NMR spectra of this compound at +263 p.p.m. (deshielded) from the usual $Cd(ClO_4)_2$ solution standard. This result was somewhat surprising in that for a 2S–2O system the resonance would normally be expected at ~ + 400 p.p.m. or greater. We decided to do a structure analysis to determine the Cd stereochemistry. The detailed discussion of the solid and solution NMR will be combined with other ^{113}Cd NMR data and published elsewhere.

Experimental. To prepare dinitratobis(1,1,3,3-tetramethyl-2-thiourea)cadmium(II), 1·32 g (0·01 mol) of 1,1,3,3-tetramethyl-2-thiourea (Sigma) was dissolved in 50 ml water and added to a like volume containing 1·54 g (0·005 ml) of $Cd(NO_3)_2.4H_2O$ (Fisher). The resulting solution was warmed gently (~ 333 K) for 15 min, allowed to cool and evaporate slowly at ambient temperature. Diffraction-quality crystals formed in 6–8 d, were collected without washing and sealed in glass capillaries.

~ 0·12 × 0·24 × 0·64 mm, Enraf–Nonius CAD-4 interfaced to a PDP 11/60 (Enraf–Nonius, 1980), D_m by flotation in CCl_4–$CHBr_3$, $h0l, l = 2n + 1$, $0k0, k = 2n + 1$ absent, faces: (101), $(\bar{1}0\bar{1})$, $(\bar{1}10)$, $(1\bar{1}0)$, (110), $(\bar{1}\bar{1}0)$, (100), $(\bar{1}00)$, absorption corrections made, transmission factors max. 0·863, min. 0·649 (Frenz, 1980), graphite monochromator, $\theta = 6{\cdot}1°$, $P = 0{\cdot}030$ in $\sigma(F_o^2) = [\sigma(I_{\rm raw})^2 + (PI_{\rm raw})^2]^{1/2}/{\rm Lp}$, $w = 1/\sigma(F_o)^2$, $F^2 > 4\,\sigma(F^2)$, 6789 independent *hkl*, ω–2θ mode, $2\theta_{\rm max} = 60°$, *hkl*, $h = -18$–18, $k = 0$–10, $l = 0$–32, 2897 reflections used, 64 unobserved with $F_{\rm min} = 13{\cdot}5$, variable scan speed starting at 4°min^{-1} 2θ, 25 general reflections in orientation matrix (checked every 24 h), 3 standard reflections every 100 reflections, decay less than 2%*I*; structure solved by heavy-atom methods (Frenz, 1980) and refined by full-matrix anisotropic least squares, anomalous-dispersion corrections with weights based upon intensity statistics (Frenz, 1980), H atoms from difference maps included but not refined, $\sum_i w_i[\,|F_o|_i - |F_c|_i]^2$ minimized; Amdahl V6 (XRAY: Stewart, 1979), f, f', f'' from *International Tables for X-ray Crystallography* (1974), largest shift 0·06 σ, average 0·01 σ, 226 variables, $R = 0{\cdot}054$, $R_w = 0{\cdot}060$, error of observations of unit weight = 0·85, final difference Fourier map qualitatively featureless.†

---

* To whom all correspondence should be addressed.

† Lists of structure factors, anisotropic thermal parameters and unrefined H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38227 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/83/030331-03$01.50

Discussion. The atomic coordinates are listed in Table 1, and important bond distances and angles in Table 2. Least-squares planes are also given in Table 2. An *ORTEP* (Johnson, 1970) drawing of the structure is shown in Fig. 1 and an *ORTEP* packing diagram in Fig. 2.

The crystal structure (Fig. 1) is made up of discrete molecules (ion triplets) with only normal van der Waals distances between them. The structure is most readily described as a distorted tetrahedral four-coordinate Cd^{II} with 2S and 2O ligands. The Cd–S distances are essentially identical at 2·497 (1) and 2·499 (2) Å and the shortest Cd–O(NO_3) distances are 2·290 (4) and 2·299 (4) Å. Normal Cd–S, Cd–O single bonds would be 2·52 and 2·14 Å respectively. As expected, the S–Cd–S angle is somewhat opened from the ideal tetrahedral angle to 124·74 (6)° and the O(11)–Cd–O(21) is closed to 92·6 (1)°. There is another set of Cd–O(NO_3) distances at 2·681 (4) and 2·686 (4) Å. However, since these are ~ 0·4 Å further away, these interactions must be very weak in terms of covalent bonding and are brought about rather by the nitrate group being oriented by the planar CNC_2 ends of the modified thiourea groups (Fig. 1) with which they are essentially parallel.

It is interesting to note that the N—O distances increase in a uniform manner depending upon the proximity of the oxygen to the Cd atom.

The C—S, C—N distances and corresponding angles in the tetramethylthiourea groups are normal for this type of metal complex. The S, C and N atoms of the thiourea group are planar well within experimental error (Table 2) but the planes defined by the terminal

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

$B_{eq} = \frac{8}{3}\pi^2 \text{ trace } \tilde{U}$.

	x	y	z	B_{eq}(Å^2)
Cd	0·24387 (2)	0·00049 (5)	0·13782 (1)	3·05 (1)
S(1)	0·13391 (9)	0·2542 (2)	0·17699 (5)	3·43 (6)
S(2)	0·1693 (1)	−0·2932 (2)	0·09165 (5)	3·68 (6)
N(11)	0·1302 (3)	0·3024 (6)	0·2977 (2)	3·2 (1)
N(12)	0·2977 (3)	0·3335 (6)	0·2621 (2)	3·0 (2)
N(21)	0·3212 (3)	−0·3029 (7)	0·0137 (2)	3·4 (2)
N(22)	0·1468 (3)	−0·3130 (6)	−0·0308 (2)	3·6 (2)
N(1)	0·3107 (4)	0·1740 (7)	0·0277 (2)	3·7 (2)
N(2)	0·3255 (3)	−0·1502 (6)	0·2567 (2)	3·5 (2)
O(11)	0·3658 (3)	0·1166 (5)	0·0756 (2)	4·1 (2)
O(12)	0·3538 (4)	0·2423 (7)	−0·0153 (2)	5·7 (2)
O(13)	0·2114 (3)	0·1461 (7)	0·0240 (2)	5·3 (3)
O(21)	0·3757 (3)	−0·0820 (7)	0·2138 (2)	4·1 (1)
O(22)	0·3742 (4)	−0·2072 (8)	0·3043 (2)	6·2 (3)
O(23)	0·2267 (3)	−0·1600 (7)	0·2480 (2)	5·4 (3)
C(11)	0·1930 (3)	0·2968 (6)	0·2506 (2)	2·5 (1)
C(21)	0·2160 (4)	−0·3008 (7)	0·0191 (2)	2·7 (1)
C(111)	0·0265 (4)	0·2088 (9)	0·2935 (3)	4·3 (3)
C(112)	0·1482 (5)	0·437 (1)	0·3479 (3)	4·8 (3)
C(121)	0·3592 (4)	0·2956 (9)	0·3215 (3)	4·4 (3)
C(122)	0·3636 (4)	0·390 (1)	0·2129 (3)	4·3 (3)
C(211)	0·4021 (4)	−0·3445 (9)	0·0640 (3)	4·3 (3)
C(212)	0·3659 (5)	−0·237 (1)	−0·0434 (3)	4·7 (3)
C(221)	0·1656 (6)	−0·430 (1)	−0·0839 (3)	5·5 (3)
C(222)	0·0355 (5)	−0·252 (1)	−0·0297 (3)	5·0 (3)

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses and least-squares planes data*

Cd–O(11)	2·290 (4)	C(111)–H(1111)	0·987 (6)
Cd–O(21)	2·299 (4)	C(111)–H(1112)	1·018 (6)
Cd–S(1)	2·497 (1)	C(111)–H(1113)	0·999 (6)
Cd–S(2)	2·499 (2)	C(112)–H(1121)	0·863 (7)
O(11)–N(1)	1·262 (6)	C(112)–H(1122)	0·987 (6)
N(1)–O(12)	1·224 (7)	C(112)–H(1123)	1·021 (7)
N(1)–O(13)	1·254 (6)	C(121)–H(1211)	0·879 (6)
O(21)–N(2)	1·272 (6)	C(121)–H(1212)	1·021 (6)
N(2)–O(22)	1·220 (6)	Cd–O(23)	2·686 (5)
N(2)–O(23)	1·234 (6)	C(121)–H(1213)	1·044 (6)
S(1)–C(11)	1·721 (4)	C(122)–H(1221)	1·059 (6)
C(11)–N(11)	1·347 (6)	C(122)–H(1222)	0·985 (7)
N(11)–C(111)	1·460 (7)	C(122)–H(1223)	1·031 (6)
N(11)–C(112)	1·465 (8)	C(211)–H(2111)	0·896 (6)
C(11)–N(12)	1·336 (6)	C(211)–H(2112)	0·990 (6)
N(12)–C(121)	1·461 (7)	C(211)–H(2113)	1·003 (6)
Cd–O(13)	2·681 (5)	C(212)–H(2121)	0·989 (7)
N(12)–C(122)	1·468 (7)	C(212)–H(2122)	1·001 (7)
S(2)–C(21)	1·729 (5)	C(212)–H(2123)	1·045 (6)
C(21)–N(21)	1·332 (6)	C(221)–H(2211)	0·905 (8)
N(21)–C(211)	1·448 (7)	C(221)–H(2212)	0·969 (8)
N(21)–C(212)	1·484 (8)	C(221)–H(2213)	1·055 (7)
C(21)–N(22)	1·322 (6)	C(222)–H(2221)	0·926 (7)
N(22)–C(221)	1·464 (8)	C(222)–H(2222)	1·007 (7)
N(22)–C(222)	1·465 (8)	C(222)–H(2223)	1·015 (7)

O(11)–Cd–O(21)	92·6 (1)	H(1121)–C(112)–H(1123)	106·6 (7)
O(11)–Cd–S(1)	110·3 (1)	H(1121)–C(112)–N(11)	113·7 (6)
O(11)–Cd–S(2)	108·9 (1)	H(1122)–C(112)–H(1123)	108·8 (6)
O(21)–Cd–S(1)	109·3 (1)	H(1122)–C(112)–N(11)	110·2 (6)
O(21)–Cd–S(2)	106·2 (1)	H(1123)–C(112)–N(11)	107·7 (5)
S(1)–Cd–S(2)	124·74 (6)	H(1211)–C(121)–H(1212)	85·4 (6)
Cd–O(11)–N(1)	105·4 (3)	H(1211)–C(121)–H(1213)	129·9 (6)
O(11)–N(1)–O(12)	121·0 (5)	H(1211)–C(121)–N(12)	94·7 (5)
O(11)–N(1)–O(13)	117·3 (5)	H(1212)–C(121)–H(1213)	125·6 (6)
O(12)–N(1)–O(13)	121·4 (5)	H(1212)–C(121)–N(12)	103·0 (5)
Cd–O(21)–N(2)	104·8 (3)	H(1213)–C(121)–N(12)	111·6 (5)
O(21)–N(2)–O(22)	120·6 (4)	H(1221)–C(122)–H(1222)	112·1 (5)
O(21)–N(2)–O(23)	117·8 (4)	H(1221)–C(122)–H(1223)	108·5 (6)
O(22)–N(2)–O(23)	121·5 (5)	H(1221)–C(122)–N(12)	104·7 (5)
Cd–S(1)–C(11)	104·2 (2)	H(1222)–C(122)–H(1223)	108·2 (5)
S(1)–C(11)–N(11)	118·6 (3)	H(1222)–C(122)–N(12)	112·8 (6)
S(1)–C(11)–N(12)	122·5 (3)	H(1223)–C(122)–N(12)	110·3 (5)
N(11)–C(11)–N(12)	118·9 (4)	H(2111)–C(211)–H(2112)	110·6 (5)
C(11)–N(11)–C(111)	121·1 (4)	H(2111)–C(211)–H(2113)	109·5 (6)
C(11)–N(11)–C(112)	121·6 (4)	H(2111)–C(211)–N(21)	103·5 (5)
C(111)–N(11)–C(112)	115·5 (5)	H(2112)–C(211)–N(2113)	110·0 (5)
C(11)–N(12)–C(121)	123·5 (4)	H(2112)–C(211)–N(21)	112·3 (5)
C(11)–N(12)–C(122)	121·8 (4)	H(2113)–C(211)–N(21)	110·8 (4)
C(121)–N(12)–C(122)	114·1 (4)	H(2121)–C(212)–H(2122)	111·7 (5)
Cd–S(2)–C(21)	104·2 (2)	H(2121)–C(212)–H(2123)	108·1 (6)
S(2)–C(21)–N(21)	120·2 (3)	H(2121)–C(212)–N(21)	110·0 (6)
S(2)–C(21)–N(22)	119·6 (4)	H(2122)–C(212)–N(2123)	105·9 (7)
N(21)–C(21)–N(22)	120·1 (4)	H(2122)–C(212)–N(21)	111·8 (5)
C(21)–N(21)–C(211)	124·2 (4)	H(2123)–C(212)–N(21)	109·2 (5)
C(21)–N(21)–C(212)	121·5 (4)	H(2211)–C(221)–H(2212)	113·4 (8)
C(211)–N(21)–C(212)	113·8 (4)	H(2211)–C(221)–H(2213)	110·7 (8)
C(21)–N(22)–C(221)	122·6 (5)	H(2211)–C(221)–N(22)	108·1 (6)
C(21)–N(22)–C(222)	121·1 (5)	H(2212)–C(221)–H(2213)	110·8 (6)
C(221)–N(22)–C(222)	114·3 (5)	H(2212)–C(221)–N(22)	104·0 (6)
H(1111)–C(111)–H(1112)	109·7 (5)	H(2213)–C(221)–N(22)	109·7 (6)
H(1111)–C(111)–H(1113)	111·3 (5)	H(2221)–C(222)–H(2222)	108·9 (7)
H(1111)–C(111)–N(11)	102·6 (5)	H(2221)–C(222)–H(2223)	108·2 (7)
H(1112)–C(111)–H(1113)	108·1 (6)	H(2221)–C(222)–N(22)	111·8 (5)
H(1112)–C(111)–N(11)	112·0 (5)	H(2222)–C(222)–H(2223)	107·7 (6)
H(1113)–C(111)–N(11)	113·0 (5)	H(2222)–C(222)–N(22)	110·6 (6)
H(1121)–C(112)–H(1122)	109·6 (7)	H(2223)–C(222)–N(22)	109·5 (6)

Planes of the form (Stewart, 1979) $Px + Qy + Rz = S$

	Plane	Maximum deviation from plane (Å)
I	S(1), C(11), N(12), N(11)	0·02 (1)
II	S(2), C(21), N(22), N(21)	0·02 (1)
III	N(1), O(11), O(12), O(13)	0·02 (1)
IV	N(2), O(21), O(22), O(23)	0·006 (2)
III, IV, Cd		0·04 (1)
V	C(11), N(12), C(121), C(122)	0·05 (1)
VI	C(11), N(11), C(112), C(111)	0·08 (1)
VII	C(21), N(21), C(212), C(211)	0·04 (1)
VIII	C(21), N(22), C(222), C(221)	0·09 (1)

Angles between planes (°)

III–IV	2·3 (1)	VII–IV	8·3 (1)
V–VI	49·4 (1)	VI–III	59·4 (1)
VII–VIII	48·7 (1)	VIII–IV	56·6 (1)
V–III	10·1 (1)		

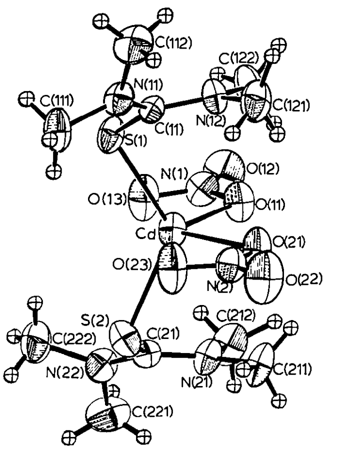

Fig. 1. An *ORTEP* (Johnson, 1970) view of the dinitratobis(tetramethylthiourea)cadmium(II) molecule. The twisting within the tetramethylthiourea ligand is readily apparent as are the parallel planes of the thiourea groups and the nitrate groups. The non-hydrogen atoms were drawn at the 50% probability level and the hydrogen atoms were drawn with an arbitrary 0·1 Å diameter.

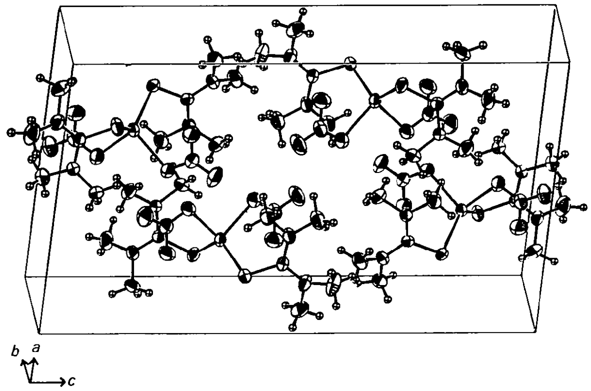

Fig. 2. An *ORTEP* view of the packing within the unit cell of dinitratobis(tetramethylthiourea)cadmium(II). The origin is in the lower left-hand corner and the axes are as indicated.

nitrogen and carbon atoms of a tetramethylthiourea group are twisted by 49·4 (1)° relative to each other, probably due to steric interference.

We view this molecule, therefore, as a distorted four-coordinate CdS_2O_2 moiety. We can only give a tentative reason for the somewhat surprising chemical shift based upon a model from data submitted for publication of other structures and ^{113}Cd NMR (Charles, Griffith, Rodesiler & Amma, 1982). In brief: the most shielded ^{113}Cd nucleus should be the gaseous Cd^{2+} closed-shell $^1S_0$ ion. Any chemical bonding involving sharing of the electron pairs will deshield this nucleus due to a mixing of orbitals. Hence even the $Cd(H_2O)_6^{2+}$ standard will be deshielded relative to the 'lone' Cd^{2+} spherical ion. Therefore 'hard' ions in the vicinity of the Cd nucleus are weakly bound to Cd and will tend to make the nucleus appear more shielded by as much as 100 p.p.m. relative to the standard. With this tentative model in mind, the observed ^{113}Cd chemical shift of the present structure is reasonable, if unexpected. Confirmation of this model and concept will come from more structural and ^{113}Cd NMR data.

This research is supported by NIH grant GM-27721. We wish to acknowledge the NSF-supported regional NMR centers at the University of South Carolina (CHE 78-18723) and Colorado State University (CHE 78-18581) for their assistance with the NMR data.

References

Bobsein, B. R. & Myers, R. J. (1981). *J. Biol. Chem.* **256**, 5313–5316.

Briggs, R. W. & Armitage, I. M. (1982). *J. Biol. Chem.* **257**, 1259–1262.

Charles, N. G., Griffith, E. A. H., Rodesiler, P. F. & Amma, E. L. (1982). *Inorg. Chem.* Submitted.

Enraf–Nonius (1980). *Data Collection Package for the CAD-4 Diffractometer* (revised for the PDP-8A, PDP-11 operation).

Frenz, B. A. (1980). *Enraf–Nonius Structure Determination Package.* Version 17 with local modification for the PDP-11/60.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Jensen, C. F., Deshmukh, S., Jakobsen, H. J., Inners, R. K. & Ellis, P. D. (1981). *J. Am. Chem. Soc.* **103**, 3659–3666.

Johnson, C. K. (1970). *ORTEP* II. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee

Linse, P., Gustavsson, H., Lindman, B. & Drakenberg, T. (1981). *J. Magn. Reson.* **45**, 133–141.

Mennitt, P. G., Shatlock, M. P., Bartuska, V. J. & Maciel, G. E. (1981). *J. Chem. Phys.* **85**, 2087–2091.

Otvos, J. D. & Armitage, I. M. (1979). *J. Am. Chem. Soc.* **101**, 7734–7736.

Rodesiler, P. F. & Amma, E. L. (1982). *J. Chem. Soc. Chem. Commun.* pp. 182–184 and references therein.

Rodesiler, P. F., Griffith, E. A. H., Ellis, P. D. & Amma, E. L. (1980). *J. Chem. Soc. Chem. Commun.* pp. 492–493 and references therein.

Sadler, P. J., Bakka, A. & Beynon, P. J. (1978). *FEBS Lett.* **94**, 315–318.

Stewart, J. M. (1979). Editor. The XRAY system. Tech. Rep. TR-445. Computer Science Center, Univ. of Maryland.