contrast to the two apical bonds of Sn to carboxylate O and amino N (Ruisi *et al.*, 1985).

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The Structure and the Solid-State ^{113}Cd NMR of Bis(2-aminomethylpyridine)dinitrato-cadmium(II)

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Abstract. $[Cd(NO_3)_2(C_6H_8N_2)_2]$, $M_r = 452.70$, monoclinic, $P2_1/c$, $a = 9.020$ (2), $b = 8.970$ (1), $c = 10.231$ (1) Å, $\beta = 101.80$ (1)°, $V = 810.3$ (4) Å^3, $Z = 2$, $D_m = 2.0$–1.8 (with decomposition), $D_x = 1.86$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 13.84$ cm^{-1}, $F(000) = 452$, $T \sim 293$ K, $R = 0.063$, 2171 observed reflections. The structure may be described as isolated bis(2-aminomethylpyridine)dinitratocadmium(II) entities separated by ordinary van der Waals distances. The Cd atom is on a crystallographic center of symmetry. The coordination polyhedron of Cd is that of a *trans* CdN$_4$O$_2$ system in which the four N atoms come from the two 2-aminomethylpyridine ligands and the O atoms are from monodentate nitrate groups. The Cd–N distances are 2.326 (2) Å (pyridine N) and 2.279 (2) Å (amino N). The Cd–O distance is 2.450 (3) Å. There is an approximately 7° tilt of the O–Cd–O line relative to the normal of the CdN$_4$ equatorial plane. The ^{113}Cd CP/MAS solid-state signal is observed at 222 p.p.m. deshielded from the 0.1 mol dm^{-3} Cd(ClO$_4$)$_2$ in D$_2$O standard.

Introduction. ^{113}Cd NMR has been shown to be a versatile tool for the observation of metal sites in a wide variety of chemical and biological compounds (Rodesiler, Turner, Charles, Griffith & Amma, 1984; Ellis, 1983, and references therein; Armitage & Otvos, 1982, and references therein). The development of solid-state cross-polarization magic-angle spinning (CP/MAS) ^{113}Cd NMR has even further enhanced the potential utility of this metal-ion probe (Ackerman, Orr, Bartuska & Maciel, 1979; Mennitt, Shatlock, Bartuska

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& Maciel, 1981). The combination of X-ray crystallography and solid-state cross-polarization magic-angle spinning offers an excellent opportunity to study and correlate metal-ion geometry with ^{113}Cd NMR chemical shift and thereby convert ^{113}Cd NMR into a much more useful chemical tool. The ultimate goal of such studies is to be able to observe the ^{113}Cd NMR signal in the solid or in solution and to be able to describe the ligands and the stereochemistry of these ligands about the Cd atom, or the stereochemistry of a metal ion which has been substituted by Cd. To this end we have been actively synthesizing compounds, determining their crystal structures, measuring the solid-state CP/MAS ^{113}Cd NMR and the solution ^{113}Cd NMR as well. We report here a portion of this ongoing research program.

Experimental. An aqueous solution containing 1·08 g (0·01 mol) 2-aminomethylpyridine (Aldrich) was added slowly with stirring to an aqueous solution of 1·54 g (0·005 mol) Cd(NO$_3$)$_2$.2H$_2$O (Fisher). The total volume of approximately 120 ml was heated gently (333 K) for 45 min, then allowed to evaporate at ambient temperature. Diffraction-quality crystals were collected after 4–5 d and protected from moisture since they are somewhat hygroscopic. The crystals were collected by gravity filtration and either sealed in thin-walled capillaries for X-ray diffraction studies or stored for NMR measurements. D_m was by flotation, but some type of decomposition occurs in the solvent mixtures of appropriate density, and three different materials are formed and hence the large range of densities. Enraf–Nonius CAD-4 diffractometer interfaced to PDP-11/60, crystal aligned by standard techniques (Enraf–Nonius, 1982). Cell dimensions determined from 25 reflections within a θ of 10°–18°. $h0l$ $l = 2n+1$, $0k0$ $k = 2n+1$ absent; crystal faces: (010), $0\bar{1}0$, (101), $(\bar{1}0\bar{1})$, $(\bar{1}01)$, $(10\bar{1})$, $(\bar{1}\bar{1}1)$, $(11\bar{1})$, (001), $(00\bar{1})$; crystal size: 0·62 × 0·22 × 0·19 mm; analytical absorption correction made (*SDP* package, see below), max., min. transmission factors 0·837, 0·563; graphite monochromator, $\theta = 6·1°$; $P = 0·071$ in $\sigma(F_o{}^2) = [\sigma(I_{raw})^2 + (PI_{raw})^2]^{1/2}/Lp$ and $w = 1/\sigma(F_o{}^2)$; data considered non-zero if F^2 greater than $4\sigma(F_o{}^2)$, 2360 independent hkl's measured in ω–2θ mode to $2\theta_{max} = 60°$ (sin $\theta/\lambda = 0·7035$ Å^{-1}), hkl range 0 to 11, 0 to 11, −12 to 12; observed variable scan speed with preliminary scan speed of 4° min^{-1} (2θ), 25 general reflections used in orientation matrix (checked every 24 h) and used for all parameter measurements; three standard reflections monitored every 100 reflections (526, $32\bar{8}$, $\bar{2}\bar{2}8$); decay less than 1% (*I*), structure solved by standard heavy-atom methods, structure refined by full-matrix least squares, anisotropic temperature factors and anomalous-dispersion corrections with weights based upon intensity statistics; function minimized $\sum_i w_i [(F_o)_i - (F_c)_i]^2$; final least squares performed on VAX-780 with f, f' and f'' for Cd^{2+} and

Table 1. *Fractional atomic coordinates with e.s.d.'s in parentheses and equivalent isotropic temperature factors*

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

	x	y	z	B_{eq}(Å^2)
Cd	0·0000	0·0000	0·0000	2·79
N(1)	−0·2544 (3)	−0·0586 (3)	−0·0751 (2)	2·45
N(2)	−0·0843 (3)	−0·0809 (3)	0·1830 (2)	2·77
C(1)	−0·3101 (3)	−0·1459 (3)	0·0096 (3)	2·57
C(2)	−0·4593 (4)	−0·1975 (4)	−0·0211 (4)	3·42
C(3)	−0·5514 (4)	−0·1556 (4)	−0·1395 (4)	3·74
C(4)	−0·4946 (4)	−0·0621 (4)	−0·2259 (3)	3·37
C(5)	−0·3455 (6)	−0·0182 (4)	−0·1906 (4)	3·06
C(6)	−0·2066 (4)	−0·1881 (4)	0·1405 (3)	3·12
N(3)	0·1398 (3)	−0·3369 (3)	0·0124 (3)	2·81
O(1)	0·0724 (3)	−0·2449 (3)	−0·0727 (2)	3·86
O(2)	0·1465 (3)	−0·3127 (3)	0·1325 (2)	4·37
O(3)	0·1993 (5)	−0·4487 (5)	−0·0247 (4)	6·07

Table 2. *Interatomic distances (Å) and angles (°) with e.s.d.'s in parentheses*

Cd–N(1)	2·326 (2)	C(1)–C(6)	1·516 (4)
Cd–N(2)	2·279 (2)	C(2)–C(3)	1·374 (5)
Cd–O(1)	2·450 (3)	C(3)–C(4)	1·390 (5)
N(1)–C(1)	1·340 (4)	C(4)–C(5)	1·377 (5)
N(1)–C(5)	1·344 (5)	N(3)–O(1)	1·262 (4)
N(2)–C(6)	1·461 (4)	N(3)–O(2)	1·237 (4)
C(1)–C(2)	1·397 (4)	N(3)–O(3)	1·233 (5)
N(1)–Cd–N(2)	74·2 (1)	C(2)–C(3)–C(4)	119·4 (3)
N(1)–Cd–O(1)	90·2 (1)	C(3)–C(4)–C(5)	118·2 (3)
N(2)–Cd–O(1)	96·8 (1)	Cd–N(1)–C(1)	113·2 (2)
N(1)–C(1)–C(2)	121·3 (3)	Cd–N(1)–C(5)	127·9 (2)
N(1)–C(5)–C(4)	122·8 (3)	Cd–O(1)–N(3)	119·8 (2)
N(1)–C(1)–C(6)	118·2 (2)	Cd–N(2)–C(6)	108·9 (2)
C(1)–N(1)–C(5)	118·9 (3)	O(1)–N(3)–O(2)	119·3 (3)
N(2)–C(6)–C(1)	112·9 (2)	O(1)–N(3)–O(3)	119·9 (3)
C(2)–C(1)–C(6)	120·5 (2)	O(2)–N(3)–O(3)	120·8 (3)
C(1)–C(2)–C(3)	119·3 (3)		

the remaining neutral atoms from Ibers & Hamilton (1974), H atoms located from difference maps and coordinates and isotropic temperature factors were refined; largest shift at end of refinement = 0·007σ, av. shift < 0·002σ, No. of variables 169; final $R = 0·0626$, $wR = 0·0599$; error of observation of unit weight = 0·993; the final difference map had a maximum of 1·70 e Å^{-3} and a minimum of −3·51 e Å^{-3}; all computer programs used were either those in the Enraf–Nonius *SDP* package (Frenz, 1982) on the PDP 11/60 or the VAX-780 with *SHELX*76 (Sheldrick, 1976). *ORTEP*II (Johnson, 1976) calculated on Amdahl V6. The atomic coordinate parameters and errors are listed in Table 1.* Selected interatomic distances and angles and errors are listed in Table 2. The experimental

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* Lists of structure factors, H-atom parameters, anisotropic thermal parameters, all distances and angles, and details of least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42692 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

conditions and equipment for the [113]Cd NMR have been described elsewhere (Charles, Griffith, Rodesiler & Amma, 1983).

Discussion. The structure may be described as made up of isolated neutral bis(2-aminomethylpyridine)-dinitratocadmium(II) species with only normal van der Waals distances between these moieties, Fig. 1. The Cd atom is on a crystallographic center of symmetry, and this demands that the molecule must be *trans*. This further demands that the four N atoms of the two 2-aminomethylpyridine ligands are coplanar with the Cd atom. The net result is an approximate tetragonally distorted octahedral Cd[II] environment. However, the O(1)—Cd—O(1') line is displaced away from the perpendicular to this plane by about 7°, Fig. 2. As expected, the Cd—N bond to the aromatic N is longer than that to the aliphatic N, 2·326 (3), 2·279 (2) Å,
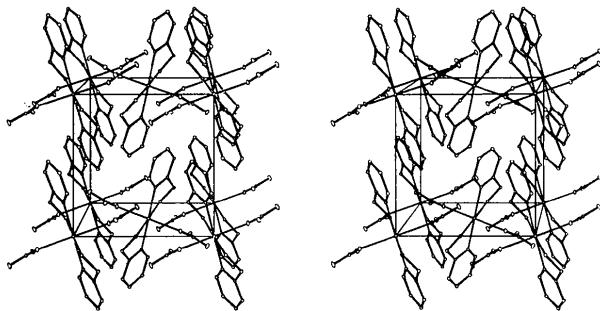
respectively. However, these are well within the range of observed Cd—N distances (Rodesiler *et al.*, 1984; Rodesiler, Charles, Griffith, Lewinski & Amma, 1986). The Cd—O(nitrate) distance of 2·450 (3) Å is consistent with that observed for other Cd—O distances in six-coordinate Cd complexes (Rodesiler *et al.*, 1984) but about 0·2 Å longer than that observed in four-coordinate complexes (Griffith, Charles, Rodesiler & Amma, 1983). All other distances and angles are the expected values. The solid-state cross-polarization magic-angle spinning (CP/MAS) [113]Cd NMR is observed at 222 p.p.m. deshielded from the 0·1*M* Cd(ClO₄)₂ in D₂O standard. No solution [113]Cd NMR spectrum was observed due to insolubility or to decomposition of the sample in most solvents. The value of 222 p.p.m. is unexpectedly high when compared to that found in what might be considered comparable systems at 51 p.p.m. deshielded (Rodesiler *et al.*, 1984). However, the configuration in the above compound is *cis* and not *trans*. The effect of such configuration differences on the [113]Cd NMR is yet to be conclusively established.

Fig. 1. An *ORTEP*II stereodrawing of the contents of the unit cell. The H atoms have been deleted for simplicity. The origin of the unit cell is in the lower left-hand corner with the *x* direction vertical, *y* horizontal and *z* directed away from the observer.
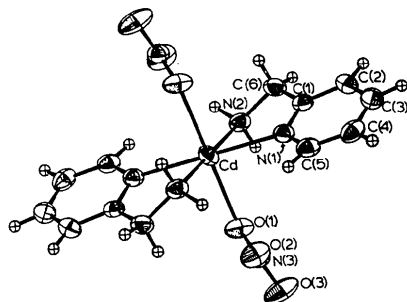

Fig. 2. An *ORTEP*II drawing of an isolated molecule of bis(2-aminomethylpyridine)dinitratocadmium(II). The atoms are drawn as indicated in Fig. 1 and only the crystallographically independent non-hydrogen atoms are indicated. The atom notation is consistent with tables and text.

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