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The Structure and CP/MAS ^{113}Cd NMR of Ephedrinium *catena*-Aqua-di-μ-chloro-chlorocadmium(II), $(C_{10}H_{16}NO)[CdCl_3(H_2O)]$*

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Abstract. $M_r = 400{\cdot}0$, $P2_1/c$, $a = 13{\cdot}686\,(2)$, $b = 7{\cdot}548\,(3)$, $c = 14{\cdot}551\,(3)$ Å, $\beta = 104{\cdot}16\,(1)°$, $V = 1457{\cdot}4\,(8)$ Å^3, $Z = 4$, $D_m = 1{\cdot}80\,(2)$, $D_x = 1{\cdot}82$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 20{\cdot}2$ cm^{-1}, $F(000) = 1132$, $T \sim 293$ K, $R = 0{\cdot}040$, 3500 reflections. The structure may be described as ephedrinium ions and a linear chain of the type $[CdCl_3(H_2O)]_n^{n-}$. The Cd atoms are octahedrally coordinated with the four equatorial halogens forming the chain with an axial chlorine atom and an axial water molecule. The bond distances and angles within the ephedrinium ion have the expected values. The Cd—Cl distances average 2·619 Å with a total variation of 0·03 Å and an e.s.d. of ±0·001 Å for each distance. The solid-state CP/MAS ^{113}Cd NMR signal is observed at 200 p.p.m. deshielded from 0·1 mol dm^{-3} $Cd(ClO_4)_2$ in D_2O standard with a half width of 18 p.p.m.

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 (Charles, Griffith, Rodesiler & Amma, 1983; Ellis, 1983). The development of solid-state cross-polarization magic-angle spinning ^{113}Cd NMR has even further enhanced the potential utility of this metal-ion-site probe (Ackerman, Orr, Bartuska & Maciel, 1979; Mennitt, Shatlock, Bartuska & Maciel, 1981). The combination of X-ray crystallography and solid-state cross-polarization magic-angle spinning (CP/MAS) 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 CP/MAS ^{113}Cd NMR and the solution ^{113}Cd NMR as well. We report here a portion of this on-going research program.

Experimental. Aqueous solution (50 ml) prepared by dissolving 2·02 g (0·01 mol) of DL-ephedrine.HCl (Sigma) and 1·14 g (0·005 mol) of $CdCl_2.\frac{1}{2}H_2O$ (Baker & Adamson) with gentle warming. pH adjusted to ~6 by dilute NaOH addition. Crystals collected without washing by gravity filtration and either sealed in thin-walled capillaries for X-ray diffraction studies or stored for NMR work. Enraf–Nonius CAD-4 diffractometer interfaced to PDP11/60, crystal aligned and intensity data collected by standard techniques (Enraf–Nonius, 1980). D_m by flotation. $h0l$ $l = 2n + 1$, $0k0$ $k = 2n + 1$ absent; crystal $0{\cdot}16 \times 0{\cdot}26 \times 0{\cdot}75$ mm; faces: (001), $(00\bar{1})$, (100), $(\bar{1}00)$, (210), $(\bar{2}10)$, $(\bar{1}\bar{1}0)$, $(1\bar{1}0)$; absorption correction, max., min. transmission factors 0·738, 0·590; graphite monochromator, $\theta = 6{\cdot}1°$; $P = 0{\cdot}030$ in $\sigma(F_o^2) = [\sigma(I_{\rm raw})^2 + (PI_{\rm raw})^2]^{1/2}/$Lp and $w = 1/\sigma(F_o)^2$; data considered non-zero if $F^2 > 4\sigma(F^2)$, 5500 independent hkl's measured in ω–2θ mode to $2\theta_{\max} = 60°$, hkl range = 0–19, 0–10, −20–18; 3500 reflections used; structure solved by standard heavy-atom methods; 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 $(26\bar{4}$, 354, $2\bar{8}2)$, decay less than 1% I; structure refined by full-matrix least squares, including 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

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* Ephedrine is α-[1-(methylamino)ethyl]benzenemethanol.

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

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

	x	y	z	$B_{\rm eq}$(Å^2)
Cd	0·01931 (1)	0·07550 (2)	0·76227 (1)	2·228 (7)
Cl(1)	0·00832 (4)	0·34012 (7)	0·87714 (4)	2·34 (2)
Cl(2)	0·03552 (5)	0·32190 (7)	0·64111 (4)	2·65 (3)
Cl(3)	0·21040 (5)	0·01759 (9)	0·81912 (5)	2·95 (3)
O(1)	0·2688 (2)	0·1254 (3)	0·4301 (1)	2·97 (7)
O(2)	−0·1596 (1)	0·1209 (3)	0·6987 (2)	3·8 (1)
N(1)	0·1765 (2)	−0·1599 (3)	0·5205 (2)	3·08 (7)
C(1)	0·3403 (2)	0·2501 (3)	0·5883 (2)	2·39 (7)
C(2)	0·3249 (2)	0·3103 (4)	0·6745 (2)	2·91 (7)
C(3)	0·3954 (3)	0·4149 (4)	0·7333 (2)	3·9 (1)
C(4)	0·4843 (3)	0·4584 (4)	0·7079 (3)	3·9 (1)
C(5)	0·5009 (3)	0·3962 (5)	0·6225 (3)	3·9 (1)
C(6)	0·4299 (2)	0·2939 (5)	0·5635 (2)	3·4 (1)
C(7)	0·2603 (2)	0·1312 (4)	0·5257 (2)	2·57 (7)
C(8)	0·2717 (2)	−0·0587 (3)	0·5636 (2)	2·52 (7)
C(9)	0·3624 (2)	−0·1537 (4)	0·5435 (3)	3·7 (1)
C(10)	0·1794 (2)	−0·3496 (4)	0·5505 (2)	3·4 (1)

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

H(1*A*)—O(2)	0·854*	C(1)—C(2)	1·387 (4)
H(2*B*)—O(2)	0·882	C(1)—C(6)	1·400 (4)
Cd—Cl(1)	2·6315 (6)	Cd—Cd$^{\rm ii}$	3·8150 (2)
Cd—Cl(2)	2·6099 (6)	C(1)—C(7)	1·521 (3)
Cd—Cl(3)	2·5803 (6)	C(2)—C(3)	1·379 (4)
Cd—O(2)	2·423 (2)	C(3)—C(4)	1·374 (5)
Cd—Cl(1$^{\rm i}$)	2·6532 (6)	C(4)—C(5)	1·396 (5)
Cd—Cl(2$^{\rm i}$)	2·5915 (6)	C(5)—C(6)	1·385 (4)
O(1)—C(7)	1·423 (3)	C(7)—C(8)	1·528 (4)
N(1)—C(8)	1·509 (3)	C(8)—C(9)	1·522 (4)
N(1)—C(10)	1·489 (4)		
Cl(1)—Cd—Cl(2)	85·16 (2)	H(2*B*)—O(2)—Cd	139·5
Cl(1)—Cd—Cl(3)	97·86 (2)	C(8)—N(1)—C(10)	114·5 (2)
Cl(1)—Cd—O(2)	85·79 (5)	C(2)—C(1)—C(6)	119·3 (2)
Cl(1)—Cd—Cl(1$^{\rm i}$)	166·91 (5)	C(2)—C(1)—C(7)	119·0 (2)
Cl(1)—Cd—Cl(2$^{\rm i}$)	98·43 (2)	C(6)—C(1)—C(7)	121·7 (2)
Cl(2)—Cd—Cl(3)	95·16 (2)	C(1)—C(2)—C(3)	120·5 (3)
Cl(2)—Cd—O(2)	83·47 (5)	C(2)—C(3)—C(4)	120·5 (3)
Cl(2)—Cd—Cl(1$^{\rm i}$)	88·89 (2)	C(3)—C(4)—C(5)	119·8 (3)
Cl(2)—Cd—Cl(2$^{\rm i}$)	167·57 (6)	C(4)—C(5)—C(6)	120·0 (3)
Cl(3)—Cd—O(2)	176·0 (1)	C(1)—C(6)—C(5)	119·9 (3)
Cl(3)—Cd—Cl(1$^{\rm i}$)	94·27 (2)	O(1)—C(7)—C(1)	112·6 (2)
Cl(3)—Cd—Cl(2$^{\rm i}$)	96·13 (2)	O(1)—C(7)—C(8)	107·1 (2)
O(2)—Cd—Cl(1$^{\rm i}$)	81·95 (5)	C(1)—C(7)—C(8)	110·1 (2)
O(2)—Cd—Cl(2$^{\rm i}$)	84·92 (5)	N(1)—C(8)—C(7)	109·3 (2)
H(1*A*)—Cd—H(2*B*)	96·8	N(1)—C(8)—C(9)	110·1 (2)
H(1*A*)—O(2)—Cd	123·6	C(7)—C(8)—C(9)	112·9 (2)
		Cl(2$^{\rm i}$)—Cd—Cl(1$^{\rm i}$)	85·08 (2)
		Cd—Cl(1)—Cd$^{\rm i}$	92·41 (2)
		Cd—Cl(2)—Cd$^{\rm i}$	94·40 (3)

Symmetry code: (i) $\bar{x}, y - \frac{1}{2}, \bar{z} + 1\frac{1}{2}$; (ii) $x, y + \frac{1}{2}, \bar{z} + 1\frac{1}{2}$.

* H-atom position not refined.

squares performed on Amdahl V6 with f, f', and f'' from Ibers & Hamilton (1974); largest Δ at end of refinement = 0·07σ, av. < 0·02σ, No. of variables = 253; final R = 0·040, R_w = 0·049; error of observation of unit weight = 1·41; H atoms located from difference electron density maps. Final difference Fourier map qualitatively featureless; all computer programs used either those in Enraf–Nonius *SDP* package (Frenz, 1982) on the PDP 11/60 or the *XRAY*79 system (Stewart, 1979) on the Amdahl V6 *ORTEP* (Johnson, 1973) calculated on Amdahl V6. The atomic coordinates and errors are listed in Table 1.* Selected interatomic distances and angles, with errors, are listed in Table 2.

Discussion. The structure may be described in terms of infinite chlorine-bridged planar chains $(\mathrm{CdCl_2})_n$ along **b** and the coordination polyhedron of Cd is completed by chlorine and water molecules protruding perpendicularly from the chain in such a manner that adjacent Cd atoms have the positions of water and chlorine reversed (Fig. 1). These chains $[\mathrm{CdCl_3(H_2O)}]_n^{n-}$ are then arranged into sheets parallel to (100) in which the individual chains are separated by ordinary van der Waals distances. The positively charged ephedrinium ions fill the space between these negatively charged sheets.

The Cd—Cl—Cd bridge is slightly asymmetric, see Table 2, with Cd—Cl—Cd bridge angles of 92·41 (2) and 94·40 (3)°. The internal Cl—Cd—Cl angles in contrast are 85·16 (2) and 85·08 (2)°. The Cd—Cl distances are the expected values (Leligny & Monier, 1974, 1975) and the non-bridging Cd—Cl distance is shorter than the others, as it should be. The Cd—O(H$_2$O) distance is long, 2·423 (2) Å, when compared to the ~2·24 Å found in carboxylic acid hydrates of Cd^{2+} (Griffith, Charles & Amma, 1982; Charles *et*

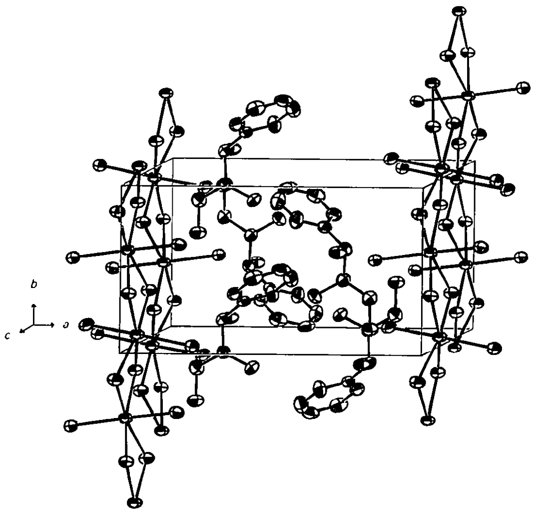

Fig. 1. An *ORTEP* drawing of the contents of the unit cell showing the ionic chain and sheet structures. These sheets can be seen at x = 0, 1 and the volume between is filled by the ephedrinium ions. The origin is in the lower back left-hand corner with axes as indicated. The hydrogen atoms have been removed for clarity.

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* Lists of structure factors, anisotropic thermal parameters, H-atom 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 39525 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

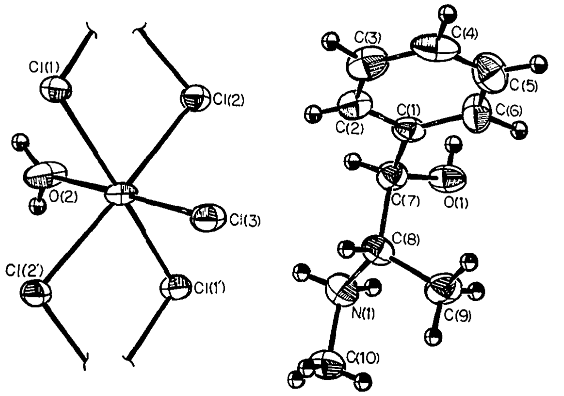

Fig. 2. An *ORTEP* drawing showing the chain structure of $[\mathrm{CdCl_3(H_2O)}]_n^{n-}$ and the isolated ephedrinium ions. The thermal ellipsoids are drawn at the 50% probability level and the H atoms are drawn with an arbitrary radius of 0·1 Å.

al., 1983) and in bis(α,α'-bipyridyl)Cd($\mathrm{H_2O}$)$\mathrm{NO_3^+}$ (Rodesiler, Turner, Charles, Griffith & Amma, 1984). It is even longer than that found in $\mathrm{CdCl_2.2\frac{1}{2}H_2O}$, ~2·33 Å (Leligny & Monier, 1974). The distances and angles in the ephedrinium ion (see Fig. 2 for atom numbering) are the expected values.

The solid-state cross-polarization magic-angle spinning (CP/MAS) ^{113}Cd NMR signal for this compound is observed at +200 (5) p.p.m., deshielded from the 0·1 mol dm^{-3} $\mathrm{Cd(ClO_4)_2}$ in $\mathrm{D_2O}$ standard, half width at half peak height in parentheses. This number is to be compared with the CP/MAS ^{113}Cd of +213 p.p.m. (5 chlorine, 1 oxygen, octahedral coordination sphere) in $\mathrm{CdCl_2.\frac{5}{2}\ H_2O}$ (Mennitt *et al.*, 1981), +187 p.p.m. (4 chlorine, 2 oxygen, octahedral coordination sphere) in the same compound and +215 p.p.m. (6 chlorine, octahedral) in $\mathrm{H_3NC_2H_4NH_3^{2+}.CdCl_4^-}$ (Honkonen, Griffith, Charles & Amma, 1984).

Although the chemical-shift differences are small, one should be able to compare directly the 5 chlorine, 1 oxygen coordination-sphere signal with other results. The trends make sense in that the stronger the donor–acceptor interaction, the greater should be the deshielding of the ^{113}Cd nucleus. The strongest covalent chemical bonding (octahedral) should be with 6 Cl (+215 p.p.m.); followed by 5 Cl, 1 water oxygen lone pair (+213 p.p.m.); 5 Cl, 1 water oxygen perhaps with a different water orientation (+200 p.p.m.), present case; 4 Cl, 2 water oxygen lone pairs (+187 p.p.m.).

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Structure of a Second Crystalline Form of a Molybdenum Trioxide–Dimethyl Sulphoxide Polymer, $\mathrm{Mo_3O_9.4(CH_3)_2SO}$

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Abstract. $M_r = 744{\cdot}3$, orthorhombic, $P2_12_12$, $a = 10{\cdot}4455\ (16)$, $b = 13{\cdot}5653\ (20)$, $c = 7{\cdot}8997\ (10)$ Å, $V = 1119{\cdot}36\ (28)$ Å^3, $D_m = 2{\cdot}20$, $D_x = 2{\cdot}21$ Mg m^{-3}, $Z = 2$, $\lambda(\mathrm{Mo}\ K\alpha) = 0{\cdot}71069$ Å, $\mu = 2{\cdot}029$ mm^{-1}, $F(000) = 732$, $T = 298$ K, $R = 0{\cdot}0338$, $R_w = 0{\cdot}0358$, 1508 observed reflections. The form of this dimorphous

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