four water-molecule bridges at each end of the organic anion. The Na^+ ions and water molecules are situated along **a**. In addition to one S atom at 3·066 (1) Å, the Na^+ ion is coordinated by five water O atoms at distances ranging from 2·382 (3) to 2·445 (2) Å forming a distorted octahedron. The other S atom of the anion ligand is outside the sodium coordination sphere, being situated 3·801 (1) Å from the Na^+ ion, which lies close to the centre of the square plane formed by O(1), O(2), O(3), $O(2^{ii})$ (O—Na—O angles range from 83·9 to 102·4°). The deviation of the Na^+ ion from this plane is 0·028 (1) Å. Each S atom accepts three hydrogen bonds from the H_2O molecules with O···S distances in the range 3·273 (2) to 3·402 (3) Å and H···S distances from 2·40 (5) to 2·69 (4) Å. Along the **bc** diagonal the structure is held together by O(3)···H—N hydrogen bonds, 2·30 (4) Å. The geometry of the organic ligand in the title compound may be compared with the corresponding parts in $Na[S_2CH(CH_2)_4].2H_2O$ (Albertsson *et al.*, 1980; Ymén, 1982), $Na[S_2CN(CH_3)_2].2H_2O$ (Oskarsson & Ymén, 1983) and $Na[S_2CN(C_3H_7)_2].5H_2O$ (Ymén, 1983). The difference in length between the S(1)—C(1) and S(2)—C(1) bonds, 3·3τ, is only possibly significant in spite of the fact that S(1) is within the sodium coordination sphere and S(2) is not. This is consistent with the ionic character of the Na—S(1) interaction. A typical feature of the compounds with ionic metal–ligand interactions is a larger ligand bite angle S—C—S (120–122°) than in the dithiocarbamates of *d*-group metals. For Na dithiocarbamates this ligand bite angle decreases very significantly as the substituents R_2 in $-S_2CNR_2$ become bulkier (Ymén, 1983). This was interpreted as the result of C—H···S intramolecular steric interactions between the substituents and the S atoms. S(1) and S(2) are pushed closer together the more bulky the substituents are. In the title compound the S(1)—C—S(2) angle [122·2 (2)°] is similar to that found in $Na[S_2CN(CH_2)_4].2H_2O$. The high degree of π conjugation in the S_2CNHC ligand fragment is reflected in the near-planarity of this fragment, the small (but significant) deviations from planarity being indicative of a small twist (2°) about the C(1)—N bond. C(2) and H(N) lie on opposite sides of the S_2CN plane at −0·037 (3) and 0·055 (7) Å, respectively.

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Structure of Polymeric Pyridinium Pentachlorodicadmate(II)*†

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Abstract. $[C_5H_6N^+.Cd_2Cl_5^-]_n$, $M_r = 482{\cdot}175n$, orthorhombic, $Pmmn$, $a = 15{\cdot}2175$ (6), $b = 3{\cdot}7897$ (2), $c = 10{\cdot}3138$ (4) Å, $V = 594{\cdot}75$ (5) Å^3, $Z = 2$, $D_x = 2{\cdot}691$ g cm^{-3}, $\lambda(\text{Cu } K\alpha_1) = 1{\cdot}54056$ Å, $\mu = 396{\cdot}8$ cm^{-1}, $F(000) = 448$, $T = 296$ (1) K. Final $R(F) = 0{\cdot}050$ for 626 counter data with $F_o^2 \geq 2\sigma(F_o^2)$. Cd atoms are on crystallographic mirror planes at $y = 0$ or $\frac{1}{2}$; Cl^- ions form distorted octahedra about them. These octahedra share edges in the **b** direction and corners in the **a** direction to give a two-dimensional polymeric network. The $C_5H_5NH^+$ ions are each hydrogen bonded to a neighboring Cl atom with the $N-H\cdots Cl^-$ linkages parallel to the z direction. The four independent Cd—Cl distances are 2·561 (1), 2·585 (2), 2·668 (2) and 2·723 (1) Å and Cl—Cd—Cl angles range from 83·38 (6) to 94·48 (10)° for *cis*-related Cl atoms.

Introduction. Among transition-metal–nucleotide complexes that have been structurally characterized, two of them are those with uridine monophosphate (UMP): $[Co_2(H_2O)_4(5'\text{-UMP})_2]_n$ (Cartwright, Goodgame, Jeeves

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& Skapski, 1977) and [Cu(5′-UMP)(2,2′-dipyridylamine)(H_2O)]$_2$ (Fischer & Bau, 1977). In an attempt to prepare a cadmium–UMP complex, a solution of $Cd(NO_3)_2$ was added to Na_2(5′-UMP) in water. Attempts to obtain crystalline material from an aqueous solution containing pyridine and *N,N*-dimethylformamide in the presence of a small amount of HCl produced crystals which were characterized by X-rays to be $[C_5H_5NH^+.Cd_2Cl_5^-]_n$. For various pyridinium halogen-coordinated metal compounds, the formations of infinite chains *via* halogen bridges have been reported for $C_5H_5NH^+.SbCl_4^-$ (Porter & Jacobson, 1970), $C_5H_5NH^+.SbBr_4^-$ (DeHaven & Jacobson, 1976), $C_5H_5NH^+.MnCl_3^-.H_2O$ (Caputo, Willet & Morosin, 1978) and $(C_5H_6N^+)_2.TeCl_6^{2-}$ (Khodadad, Viossat, Toffoli & Rodier, 1979). Results of the present study provide additional information concerning polymeric structures involving octahedral cadmium and pyridinium ions.

Experimental. A solution of $Cd(NO_3)_2$ (0·106 g in 0·7 ml of water) was added to Na_2(5′-UMP) (0·184 g in 30 ml of water). The mixed solution (pH 6·8) was stirred and left at room temperature for two weeks and then the precipitate was collected by filtration and washed with cold water. Yield: 0·158 g. The test for cadmium (Feigl, Anger & Oesper, 1972) in this dried powder was positive. After attempts to crystallize this Cd-containing powder from aqueous solution failed, the powder was dissolved in 1·05 ml of water containing 0·3 ml of pyridine plus 0·5 ml of *N,N*-dimethylformamide. To increase its solubility, 25 μl of 1 *M* HCl was also added. The solution was then dried under reduced pressure at 333 K. Upon cooling, the formation of needle crystals was observed.

Two possible space groups and the approximate unit-cell parameters were established from Weissenberg and precession photographs. A crystal with dimensions 0·04 × 0·07 × 0·43 mm was mounted on a Picker four-circle diffractometer with **b** (the longest dimension of the crystal) nearly parallel to the φ axis of the diffractometer, and lattice parameters were refined by a least-squares method from angle measurements of 12 strong reflections in the 2θ range 101–124° (Busing, Ellison, Levy, King & Roseberry, 1968). Intensity data were collected by θ–2θ step scans in the 2θ range 1–132°. Ranges of *h, k, l*: 0 to 18, 0 to 4, 0 to 12, respectively. Two standards were measured for every 35 reflections: variation ~1%. Absorption corrections were based on an azimuthal scan of reflection 020. Ratio of minimum and maximum transmission factors was 0·781. Maximum mosaic spread of the crystal specimen was estimated to be 0·5°. Of the 644 unique nonzero reflections 18 reflections with $F_o^2 < 2\sigma(F_o^2)$ were excluded from the final least-squares refinement.

At the beginning of the analysis, the composition of the compound was not known. Interpretation of a Patterson map gave the position of the Cd atom. Based on this, the Cl atoms and the six-membered-ring atoms were readily found. Although all H atoms were located from a difference-Fourier map [using the program *ORFFP*3 (Levy, 1977)], they were difficult to refine, and they were therefore constrained* in the least-squares refinement with the program *ORXFLS*4, an updated version of *ORFLS* (Busing, Martin & Levy, 1962). Scattering factors were those of Cromer & Waber (1974); anomalous-scattering corrections for Cd ($f' = -0\cdot079$, $f'' = 4\cdot653$) and Cl ($f' = 0\cdot348$, $f'' = 0\cdot702$) were taken from Cromer (1974).

Since there was ambiguity in choosing the correct space group, least-squares refinements were carried out for the two different space groups: *Pmmn* and *Pm*2$_1$*n*. All refinements were based on F^2, the function minimized being $\sum w|F_o^2 - s^2F_c^2|^2$, where the weights w are reciprocals of $\sigma_c^2(F_o^2) + (0\cdot06F_o^2)^2$. Here σ_c is the standard error from counting statistics and s is the scale factor. The $wR(F^2)$ value obtained for the centrosymmetric space group *Pmmn* was 0·1393, higher than the 0·1312 obtained for the non-centrosymmetric space group *Pm*2$_1$*n*. But the refinement assuming the non-centrosymmetric space group† led to poor convergence, and atoms N and C(3) moved to positions 0·08 (9) and 0·45 (7) Å out of the plane formed by the other atoms of the pyridine ring, a result which is stereochemically unrealistic. For this reason the results obtained assuming the centrosymmetric space group *Pmmn* are presented in this paper. The refinement was carried out until all Δ/σ became negligible, the final $R(F)$, $R(F^2)$ and S being 0·050, 0·080 and 2·115, respectively. The final difference-Fourier map showed a maximum $\Delta\rho$ of 2·7 e Å^{-3} near the Cd atom. Distances and angles were calculated with program *ORFFE*4 (Busing, Martin & Levy, 1964). Figures were prepared with program *ORTEP*II (Johnson, 1976).

Discussion. Positional and isotropic temperature factors (or their equivalents) are listed in Table 1.‡ The arrangement of molecules in the unit cell is shown in Fig. 1. The most interesting feature of the structure is the polymeric two-dimensional network formed by the

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* Each H atom was constrained to be 1·0 Å from the C or N atom to which it is attached, and it was further assumed that each of them lies on a plane consisting of the C or N atom and the two adjacent ring atoms in a bisecting position. The isotropic temperature factor of each H atom was assumed to be $1 + B_{eq}$, where B_{eq} is the equivalent isotropic temperature factor of the non-H atom to which it is bound.

† For the non-centrosymmetric space group, only y of Cd was fixed at 0 and y's of other atoms were allowed to vary.

‡ Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44121 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional and isotropic thermal parameters*

The e.s.d.'s given in parentheses in this table and in the text correspond to the least-significant digits of the parameters. The equivalent isotropic temperature factors for non-H atoms were calculated from the corresponding anisotropic thermal parameters and unit-cell parameters by the relation $B_{eq} = \frac{4}{3}(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2)$ (Hamilton, 1959).

	x	y	z	B_{eq} or B(Å^2)
Cd	0·16746 (4)	0	0·37825 (6)	2·49 (4)
Cl(1)	0·3414 (1)	0	0·4401 (2)	2·23 (6)
Cl(2)	0	0	0·3533 (5)	5·31 (15)
Cl(3)	0·1922 (2)	0·5	0·2117 (2)	2·77 (6)
N	0	0	0·0229 (20)	8·5 (10)
C(1)	0·0737 (13)	0	−0·0409 (19)	7·5 (6)
C(2)	0·0771 (8)	0	−0·1744 (13)	3·8 (3)
C(3)	0	0	−0·2379 (16)	4·1 (5)
H(N)	0	0	0·120	9·5
H(1)	0·130	0	0·009	8·5
H(2)	0·134	0	−0·222	4·8
H(3)	0	0	−0·335	5·1

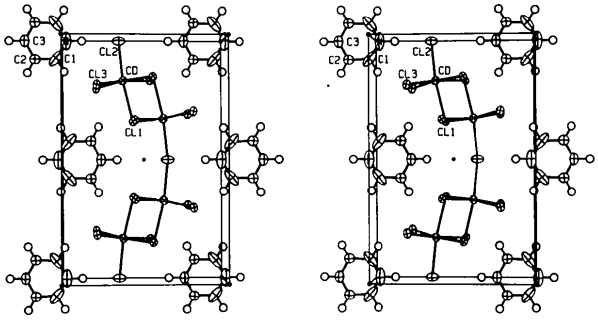

Fig. 1. A stereoscopic view down the b axis showing the packing. The origin of the unit cell is in the upper left rear corner. The a axis is vertical, and the c axis is horizontal. The crystallographic mirror planes on a and b are at $x = 0$ and $y = 0$, respectively; the n-glide plane is at $z = \frac{1}{2}$, and the center of inversion is located at $x = \frac{1}{4}$, $y = \frac{1}{4}$ and $z = 0$. Here and in Fig. 2 thermal ellipsoids enclose 50% probability.

$Cd_2Cl_5^-$ anions. The Cd atom is on a crystallographic mirror plane at $y = 0$. It is surrounded by six Cl atoms that form a distorted octahedron which is linked to the adjacent octahedra in the **b** direction by sharing Cl···Cl edges, thus forming a chain of fused octahedra. These octahedra are further related to adjacent chains by centers of inversion and the two fused chains are joined by sharing Cl(2) atoms to form a two-dimensional polymeric network, in a way similar to the structure of $C_5H_5NH^+.MnCl_3^-.H_2O$ (Caputo, Willett & Morosin, 1978). The $C_5H_5NH^+$ ions are each bonded to the neighboring Cl(2) atom at $x = y = 0$ (or $x = y = \frac{1}{2}$) *via* an N–H···Cl linkage parallel to the c axis.

The geometry around the Cd atom and the crystallographically independent Cd–Cl and Cl···Cl distances are shown in Fig. 2. It should be noted that Cl(3^i) and Cl(1^{iii}) are related to Cl(3) and Cl(1^{ii}), respectively, by the translation in the **b** direction. In this structure, the Cd–Cl distances range from 2·561 (1) Å for Cd–Cl(2) to 2·723 (1) Å for Cd–Cl(1). These values can be compared with 2·63 Å reported for octahedral $[CdCl_6]^{4-}$ (Bergerhoff & Schmitz-Dumont, 1956). The Cl–Cd–Cl (Cl atoms *cis* to each other) angles have values in a range of 83·38 (6) to 93·48 (10)°. Other bond lengths and angles of the octahedron as well as those of the $C_5H_5NH^+$ ion are listed in Table 2.

The $C_5H_5NH^+$ ion is planar with point group $2mm$ C_{2v}. The H(N) atom appeared to be slightly disordered in the difference-Fourier map with an x coordinate not exactly zero. However, from a practical point of view this problem was not pursued further, and it was assumed to be on the twofold axis at $x = y = 0$ (see above).

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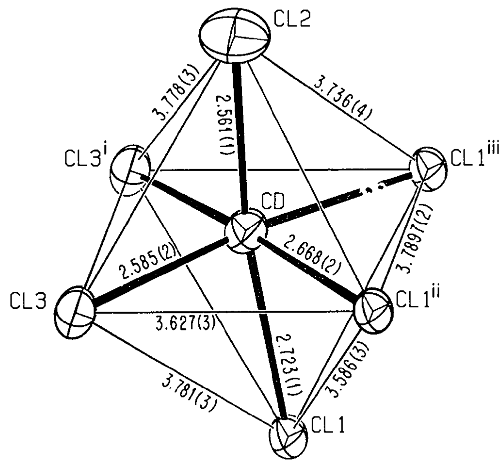

Fig. 2. The coordination around the Cd atom, showing a distorted octahedral arrangement and crystallographically independent Cd–Cl and Cl···Cl distances. Symmetry code: (i) $x, y-1, z$; (ii) $\frac{1}{2}-x, \frac{1}{2}+y, 1-z$; (iii) $\frac{1}{2}-x, -\frac{1}{2}+y, 1-z$.

Table 2. *Selected bond lengths* (Å) *and angles* (°)

N–C(1)	1·30 (2)	N···Cl(2)	3·41 (2)
C(1)–C(2)	1·38 (2)	H(N)···Cl(2)	2·407 (5)
C(2)–C(3)	1·34 (1)		
Cl(1)–Cd–Cl(1^{ii})	83·38 (6)	Cl(1^{ii})–Cd–Cl(1^{iii})	90·50 (7)
–Cl(1^{iii})	83·38 (6)	Cl(1^{iii})–Cd–Cl(3^i)	87·33 (5)
–Cl(3)	90·80 (7)	Cl(3^i)–Cd–Cl(3)	94·28 (7)
–Cl(3^i)	90·80 (7)	Cl(3)–Cd–Cl(1^{ii})	87·33 (5)
–Cl(2)	172·2 (1)	Cl(1^{ii})–Cd–Cl(3^i)	173·99 (7)
Cl(2)–Cd–Cl(1^{ii})	91·16 (9)	Cl(1^{iii})–Cd–Cl(3)	173·99 (7)
–Cl(1^{iii})	91·16 (9)		
–Cl(3)	94·48 (10)	C(1)–N–C(1^{iv})	119 (2)
–Cl(3^i)	94·48 (10)	N–C(1)–C(2)	123 (2)
		C(1)–C(2)–C(3)	117 (1)
		C(2)–C(3)–C(2^{iv})	122 (2)

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

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Bis(cyclooctene)copper(I) Trifluoromethanesulfonate

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Abstract. $[Cu(C_8H_{14})_2]CF_3SO_3$, $M_r=433{\cdot}01$, orthorhombic, $P2_12_12_1$, $a=5{\cdot}340\,(1)$, $b=16{\cdot}600\,(5)$, $c=22{\cdot}370\,(5)$ Å, $V=1983{\cdot}0\,(8)$ Å^3, $Z=4$, $D_x=1{\cdot}450$ g cm^{-3}, $\lambda(\text{Mo}\ K\alpha)=0{\cdot}71073$ Å, $\mu=12{\cdot}4$ cm^{-1}, $F(000)=904$, $T=295$ K, final $R=0{\cdot}0388$ for 1481 reflections $[I>2{\cdot}5\sigma(I)]$. The structure consists of chains, parallel to the short a axis, of Cu(cyclooctene)$_2^+$ cations [Cu—(C=C) = 2·05 Å ave.] connected by bridging trifluoromethanesulfonate anions with one short [2·049 (4)] and one long [2·433 (4) Å] Cu—O contact.

Introduction. Copper(I) salts have been used extensively as catalysts for photochemical transformations of olefins (*e.g.* Kropp, 1979; Salomon, 1983; Moggi, Juris, Sandrini & Manfrin, 1981, 1984; Hennig, Rehorek & Archer, 1985); reactions observed include *cis*⇌*trans* isomerization, skeletal rearrangement, and di-and trimerizations. Although these latter reactions have been postulated to occur in the coordination sphere of the copper ion, implying the presence of Cu(olefin)$_2^+$ and Cu(olefin)$_3^+$ complexes under reaction conditions, the number of such complexes reported to date is very limited. In fact, the only compounds containing more than one C=C π bond coordinated to a single Cu atom that have been structurally characterized are Cu_2Cl_2(*trans*-cyclooctene)$_3$ (Ganis, Lepore & Martuscelli, 1970), [CuCl(1,5-cyclooctadiene)]$_2$ (Van den Hende & Baird, 1963) and possibly [CuCl(1,3,5,7-cyclooctatetraene)]$_n$ (Baenziger, Richards & Doyle, 1964). However, Evers (1979) obtained evidence for the formation of several Cu(olefin)$_n^+$ complexes in solution.

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