Discussion. The atomic parameters are listed in Table 1,* interatomic distances and angles in Table 2. Fig. 1 is a view of the molecule and Fig. 2 shows the packing.

The structure consists of binuclear units, with the bridging oxo group O(3) located on the twofold axis passing through $0, y, \frac{1}{4}$. The symmetry-related halves of the molecule display pseudo-octahedral geometry at Mo atoms, with a *fac* stereochemistry adopted by the bridging and terminal oxo groups. The remaining positions are occupied by the amine-N and mercapto-S donors of the tridentate ligands. In common with most structures of this type, the N donors are located pseudo-*trans* to the terminal oxo groups, while the S donor occupies a position *trans* to the less strongly π-bonding bridging oxo group.

Two significant features of the structure are the Mo—O(3)—Mo' angle of 147·0 (5)° and the N(2)···O(2')$(x, y, \frac{1}{2}-z)$ close contact of 3·00 (1) Å, suggesting some degree of intramolecular hydrogen bonding. Short intermolecular contacts C(3)—H···O(1)$(\frac{1}{2}+x, \frac{1}{2}+y, z)$ of 2·44 (1) Å may conform to criteria for hydrogen bonding and thus make a significant contribution to the overall molecular packing and conformation (Berkovitch-Yellin & Leiserowitz, 1984).

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* List of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42042 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The structure is similar to that determined for [Mo2O5{Me2NCH2CH2NHCH2C(Me2)S}2], which was reported during the course of our investigations (Marabella, Enemark, Miller, Bruce, Pariyadath, Corbin & Stiefel, 1983). This analogue exhibits an angle of 143·8 (3)° at the bridging oxo group, with average Mo—O(bridging) and Mo—O(terminal) distances of 1·923 (8) and 1·713 (9) Å, respectively. Other structural parameters correspond closely to those observed for the title structure.

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Synthesis and Structure of cis-Tetrakis(acetamidine)carbonatocobalt(III) Chloride Dihydrate, [Co(CO3)(C2H6N2)4]Cl.2H2O at 117 K

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Abstract. $M_r = 422 \cdot 76$, monoclinic, $C2$, $a = 16 \cdot 475$ (4), $b = 9 \cdot 176$ (2), $c = 12 \cdot 421$ (3) Å, $\beta = 101 \cdot 52$ (2)°, $V = 1839 \cdot 9$ (8) Å^3, $Z = 4$, $D_x = 1 \cdot 526$ (1) Mg m^{-3}, Cu $K\alpha$, $\lambda = 1 \cdot 54184$ Å, $\mu = 9 \cdot 3$ mm^{-1}, $F(000) = 839 \cdot 8$, $T = 117$ (2) K, final $R = 0 \cdot 038$ for 1257 reflections. The crystals of the title compound formed by evaporation in air of a methanolic solution of CoCl$_2$ and acetamidine contain complexes of cis-tetrakis(acetamidine)carbonatocobalt(III) ions. The Co—O distances within the complex ion, 1·918 (6) and 1·933 (5) Å, and the Co—N distances ranging from 1·913 (6) to 1·942 (6) Å agree with those found in related cis-carbonato complexes of Co^{III}.

Introduction. The present study is part of a research project on synthetic and structural studies of acetamidine metal complexes (see also Norrestam, 1984a). So far, the study by Stephenson (1962) on a compound expected to be bis(acetonitrile)tetraammineplatinum(II) chloride monohydrate but shown by the

Table 1. *Experimental information*

Crystal color and shape	Red violet, prismatic
Crystal size	$0.045 \times 0.035 \times 0.175$ mm
Diffractometer	CAD-4
Determination of cell parameters	
Number of reflections used	11
θ range of reflections used	$5.9-19.6°$
Cell parameters at 293 K	$a = 16.560$ (4), $b = 9.229$ (2),
	$c = 12.517$ (5) Å, $\beta = 101.38$ (2)°
Intensity-data collection	
Max. $\sin\theta/\lambda$	0.625 Å^{-1}
Range of h, k and l	$\overline{20},0,0$ to $20,11,15$
Standard reflections	022, 400
Intensity variation	$<4\%$
Measured reflections	2125
Unique reflections	1954
Observed reflections	1257
Criterion for observed reflections	$\sigma/I < 0.2$
R_{Int}	0.018
Absorption correction	
Min. and max. transmission	$0.21-0.60$
Structure determination technique	Heavy atom
Determination of H atoms	$\Delta\rho$ map
Structure refinement	
Function minimized	$\sum w(\Delta F)^2$
Anisotropic model for	Nonhydrogens
Isotropic model for	Hydrogens
Parameters constrained for	Hydrogens
Number of parameters	294
Weighting scheme	$1/[\sigma^2(F_o) + 0.0001\,F_o^2]$
Final R	0.038
Final wR	0.044
Max. final Δ/σ	0.15
Max. and min. $\Delta\rho$	0.46, -0.61 e Å^{-3}

structural investigation to be bis(acetamidine)-diammineplatinum(II) chloride monohydrate is the only example where an acetamidine metal complex has been synthetized and characterized by X-ray diffraction techniques. Recently, Crossland & Grevil (1981) have designed an easy synthetic procedure to obtain acetamidine. With pure acetamidine available in large amounts, the possibilities of preparing new metal complexes have increased. In the first study on the synthesis of metal complexes (Norrestam, 1984a) it was shown that acetamidine could undergo a self-condensation reaction, possibly under the influence of nickel ions, to give a bidentate ligand N-acetimidoyl-acetamidine. In the present study a true acetamidine complex has been obtained although the experimental conditions are similar. Thus, the specimen was prepared by simply evaporating a methanolic solution of cobalt(II) chloride hexahydrate and acetamidine. As has been shown earlier, acetamidine, which is a strong base, might under these circumstances react with atmospheric carbon dioxide (Norrestam, 1984b). This also occurs in the present case and a cis-tetrakis-(acetamidine)carbonatocobalt complex is formed.

Experimental. Red violet crystals of the title compound were prepared by allowing a methanolic solution of $CoCl_2.6H_2O$ and acetamidine with the molar ratio 1:6 to evaporate in air.

Details on the X-ray diffraction data collection which was carried out using a conventional low-temperature device (nitrogen-gas-stream system) are given in Table 1. The origin along the polar axis was defined by keeping the y coordinate of Co fixed to 0. To determine the absolute configuration, a model consisting of only nonhydrogen atoms, all isotropic except for Co and Cl (102 parameters) without f'' corrections was refined. The parameters obtained were used in two structure factor calculations without and with inverted signs of the f'' corrections. The R (and wR) values of 0·100 and 0·084 (0·125 and 0·105) obtained respectively for the two models indicated that the latter was the correct one, as the α value (see *e.g.* Rogers, 1981) becomes negligible.

Information on the structure determination is given in Table 1. In refinement of the final model the hydrogen positions were constrained (Sheldrick, 1976) to give bond distances to the non-hydrogen atoms of 1·0 (1) Å. The isotropic hydrogen thermal parameters were kept equal within each acetamidine molecule. Atomic scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1974). Programs used were *SHELX76* (Sheldrick, 1976) and *XTAPL* (Norrestam, 1982).*

Discussion. Atomic coordinates are listed in Table 2. The crystal structure, which contains discrete cis-tetrakis(acetamidine)carbonatometal ions, chloride ions and crystal water molecules, is held together by an extensive hydrogen-bond network. In this network, indicated in Fig. 1, the N atoms of the acetamidine molecules and the water O atoms are hydrogen-bond donors. The carbonate oxygens, the chlorine and the water oxygens are hydrogen-bond acceptors.

The Co ions are octahedrally coordinated by two of the O atoms from one carbonate ion and by the imino N atoms of four acetamidine molecules. The Co—O distances 1·918 (6) and 1·933 (5) Å as well as the Co—N distances ranging from 1·913 (6) to 1·942 (6) Å (Table 3) are typical for those formed in other nitrogen-coordinated cis-carbonato low-spin complexes of Co^{III} (Healy, Kennard, Smith & White, 1981; Niederhoffer, Martell, Rudolf & Clearfield, 1982). Evidently the cobalt ions have been oxidized from divalent to trivalent during the evaporation in air. This is in accordance with the well-known ligand-field stabilization of low-spin Co^{III} (see *e.g.* Rock, 1968).

The carbonate ion is planar, root mean square deviation (r.m.s.d.) of the four atoms from a least squares (LS) plane of 0·004 Å. The uneven distribution

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Table 2. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{Å}^2 \times 10^4$) estimated as $\frac{1}{3}$ trace U

|	x	y	z	U_{eq}
Co	1285 (1)	0	2253 (1)	156 (3)
Cl	3442 (2)	2094 (3)	4709 (2)	302 (6)
O(w1)	0	4927 (10)	5000	347 (26)
O(w2)	0	4328 (8)	0	254 (25)
O(1)	1144 (3)	−99 (7)	672 (4)	180 (16)
O(2)	1148 (3)	1902 (7)	1602 (4)	215 (17)
O(3)	994 (3)	2024 (7)	−262 (4)	248 (18)
C	1094 (5)	1341 (9)	610 (7)	223 (25)
N(1a)	2468 (4)	204 (8)	2423 (5)	193 (19)
N(2a)	2739 (4)	−1432 (8)	1101 (6)	304 (24)
C(1a)	2997 (5)	−463 (9)	1919 (7)	226 (25)
C(2a)	3908 (5)	−166 (11)	2207 (7)	302 (30)
N(1b)	1423 (4)	479 (7)	3778 (5)	184 (19)
N(2b)	589 (4)	2486 (7)	3684 (6)	280 (23)
C(1b)	1135 (5)	1564 (9)	4244 (7)	267 (26)
C(2b)	1375 (5)	1832 (11)	5470 (7)	331 (29)
N(1c)	87 (4)	−125 (8)	2041 (5)	205 (20)
N(2c)	−184 (4)	−1464 (9)	3512 (6)	491 (24)
C(1c)	−435 (5)	−754 (9)	2545 (7)	205 (26)
C(2c)	−1346 (5)	−709 (11)	2101 (7)	343 (31)
N(1d)	1433 (4)	−2030 (7)	2658 (5)	195 (21)
N(2d)	788 (4)	−3075 (8)	1011 (6)	309 (23)
C(1d)	1194 (5)	−3167 (8)	2072 (6)	189 (24)
C(2d)	1361 (5)	−4670 (9)	2516 (7)	302 (31)
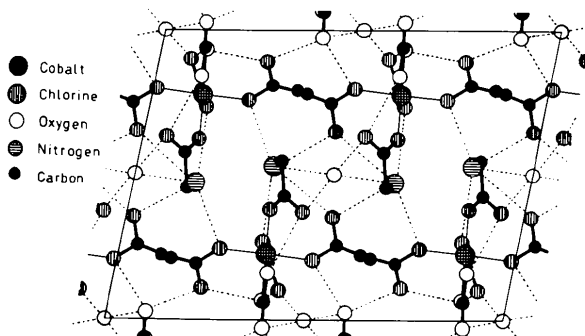
Fig. 1. Projection of the crystal structure down the *b* axis (*a* vertical and *c** horizontal).

Table 3. Bond distances (Å) and angles (°)

The asterisks indicate that the values were obtained by averaging over the four independent acetamidine molecules.

Co—O(1)	1·933 (5)	C—O(1)	1·325 (10)
Co—O(2)	1·918 (6)	C—O(2)	1·322 (10)
Co—N(1a)	1·927 (5)	C—O(3)	1·234 (9)
Co—N(1b)	1·913 (6)	C(1)—N(1)*	1·298 (8)
Co—N(1c)	1·942 (6)	C(1)—N(2)*	1·348 (7)
Co—N(1d)	1·932 (6)	C(1)—C(2)*	1·499 (6)
O(1)—Co—O(2)	68·5 (2)	N(1a)—Co—N(1b)	87·2 (2)
O(1)—Co—N(1a)	91·7 (2)	N(1a)—Co—N(1d)	89·6 (3)
O(1)—Co—N(1c)	86·9 (2)	N(1b)—Co—N(1c)	93·7 (2)
O(1)—Co—N(1d)	101·7 (2)	N(1b)—Co—N(1d)	88·8 (3)
O(2)—Co—N(1a)	89·4 (2)	N(1c)—Co—N(1d)	92·9 (3)
O(2)—Co—N(1b)	100·9 (2)	N(1)—C(1)—N(2)*	121·9 (2)
O(2)—Co—N(1c)	88·0 (2)	N(1)—C(1)—C(2)*	121·8 (2)
		N(2)—C(1)—C(2)*	116·2 (2)

of the C—O bond distances (about 1·32 Å for the two metal coordinating oxygens and 1·24 Å for the non-coordinating one) and of the O—C—O angles is characteristic of carbonate ions acting as bidentate ligands (Krishnamurty, Harris & Sastri, 1970; Nieder-hoffer *et al.*, 1982).

The nonhydrogen atoms of the acetamidine molecules are planar with r.m.s.d.'s from LS planes ranging from 0·003 to 0·006 Å. The average bond distances 1·298 (8), 1·348 (7) and 1·499 (6) Å for the C—N(1), C—N(2) and C(1)—C(2) bonds respectively agree well with those [1·298 (1), 1·344 (1) and 1·502 (1) Å] observed in pure acetamidine (Norrestam, Mertz & Crossland, 1983). The bond angles are, however, affected by coordination effects in the present structure. Thus, the N(1)—C(1)—N(2) angle has decreased to 121·9 (2)° from 125·5 (1)° in pure acetamidine, and the N(1)—C(1)—C(2) angle has increased to 121·8 (2)° from 118·8 (1)°.

The geometry of the *cis*-tetrakis(acetamidine)-carbonatocobalt(III) ion is shown in Fig. 2. The three principal LS planes through the coordination octa-hedron, *viz* the planes defined by (I): Co, O(1), O(2), N(1b), N(1d); (II): Co, O(1)*, N(1a), N(1b), N(1c); (III): Co, O(2)*, N(1a), N(1c), N(1d) (atoms marked with an asterisk have been given zero weights in the calculations) form angles ranging from 87 (1) to 92 (1)° with each other. The r.m.s.d.'s for the three planes are 0·006 to 0·017 Å. The irregularity of the Co coordination octahedron caused by the carbonate ion is indicated by the fact that the O(1) and O(2) atoms deviate significantly, 0·30 (1) Å, from the planes II and III respectively. The Co atom deviates only slightly, 0·004 to 0·014 Å, from the LS planes through the acetamidine molecules. These planes form interplanar angles with the principal planes I, II and III that deviate from 180° by 22 (1) to 44 (1)°. The carbonate ion is
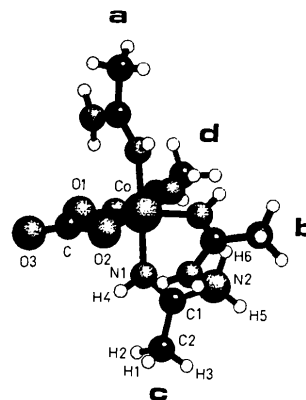

Fig. 2. Raster-plot representation (Norrestam, 1981) of the structure of the *cis*-tetrakis(acetamidine)carbonatocobalt ion and the atomic labels used.

rather coplanar with the principal plane I [interplanar angle 2 (1)°].

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Structure of a Bromo-Bridged One-Dimensional Pd^{II}–Pd^{IV} Mixed-Valence Complex, catena-μ-Bromo-bis(ethylenediamine)palladium(II,IV) Diperchlorate, $[Pd(C_2H_8N_2)_2][PdBr_2(C_2H_8N_2)_2](ClO_4)_4$

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Abstract. $M_r = 1010.80$, orthorhombic, *Imcb*, $a = 10.814$ (1), $b = 13.608$ (2), $c = 9.663$ (4) Å, $V = 1422.0$ (3) Å³, $Z = 2$, $D_x = 2.38$, $D_m = 2.39$ Mg m⁻³, $\lambda(Mo\,K\alpha) = 0.7107$ Å, $\mu(Mo\,K\alpha) = 4.677$ mm⁻¹, $F(000) = 988$, room temperature, $R = 0.038$, $wR = 0.050$ for 1016 observed reflections $[|F_o| > 3\sigma(F_o)]$. The crystal comprises linear chains, ···Pd^{II}···Br—Pd^{IV}—Br, parallel to the *a* axis, where tetragonal $[PdBr_2(en)_2]^{2+}$ and square-planar $[Pd(en)_2]^{2+}$ units are stacked alternately with bromo bridges. The Pd^{IV}—Br and Pd^{II}···Br distances along the chain are 2.496 (1) and 2.911 (1) Å, respectively. The ratio between Pd^{IV}—Br and Pd^{II}···Br distances is 0.86, which is larger than that of the chloro analog (0.77).

Introduction. Halogen-bridged one-dimensional M^{II}–M^{IV} mixed-valence complexes (M=Pt, Pd and Ni) having the structure
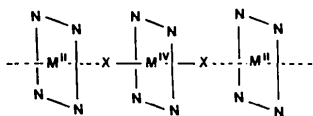
have attracted much interest from the viewpoint of low-dimensional compounds (Miller & Epstein,

1976). Their solid-state physical properties such as electronic absorption and emission spectra, and electrical conductivity, have been studied as functions of bridged halogens, metals, in-plane ligands and counter anions (Matsumoto, Yamashita & Kida, 1978a; Hamaue, Aoki, Yamashita & Kida, 1981; Yamashita, Matsumoto & Kida, 1978; Yamashita, Nonaka, Kida, Hamaue & Aoki, 1981; Tanino & Kobayashi, 1983; Yamashita & Ito, 1984). For an understanding of the physical properties, structural parameters along the linear chain are of fundamental importance. In this paper, we describe the structure of the title compound. Recently, the structure of its chloro analog, $[Pd(en)_2][PdCl_2(en)_2](ClO_4)_4$, was reported (Beauchamp, Layek & Theophanides, 1982).

Experimental. Golden needles elongated along the *a* axis recrystallized from dilute perchloric acid. D_m by flotation in CHBr₃/CHCl₃. Crystal $0.50 \times 0.30 \times 0.22$ mm. Rigaku AFC-5 diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Unit-cell dimensions by least-squares fit of 50 2θ values ($25° < 2\theta < 30°$). Intensities in the range $2\theta < 65°$ measured with θ–2θ scan technique. $h\,0\rightarrow16$, $k\,0\rightarrow20$, $l\,0\rightarrow14$. Three reference reflections monitored periodically showed no significant intensity deterioration. 2933 unique reflections measured. Intensity data corrected for Lorentz–polarization factors and for absorption. Structure solved by conventional heavy-atom method and refined

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