l'uranium, ne débute qu'au-delà de 423 K. Les étapes ultérieures correspondent à la dégradation de la chaîne carbonée.

Cette évolution, qui confirme l'existence de deux types de molécules d'eau, est en bon accord avec le spectre de diffraction X de poudre en fonction de la température qui montre que, jusque 413 K, la structure n'est pas affectée par la déshydratation. Au-delà de cette température, le spectre subit une première modification accompagnant le départ des molécules d'eau coordinées. L'altération de la chaîne moléculaire qui intervient vers 483 K se traduit par la formation d'une phase amorphe.

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The Structure of Silver Pefloxacin, an Antibiotic Related to Nalidixic Acid

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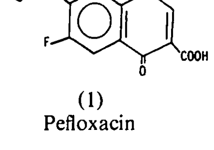
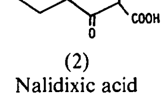
Abstract. Silver(I) 1-ethyl-6-fluoro-1,4-dihydro-7-(4-methyl-1-piperazinyl)-4-oxo-3-quinolinecarboxylate tetrahydrate, $Ag[C_{17}H_{19}FN_3O_3].4H_2O$, $M_r = 512\cdot31$, triclinic, $P\bar{1}$, $a = 8\cdot7146\,(9)$, $b = 9\cdot8853\,(11)$, $c = 13\cdot8115\,(18)$ Å, $\alpha = 69\cdot17\,(1)$, $\beta = 67\cdot54\,(1)$, $\gamma = 84\cdot69\,(1)°$, $V = 1026\cdot4\,(2)$ Å^3, $D_x = 1\cdot658$ Mg m^{-3}, $Z = 2$, $\lambda(\text{Mo}\,K\alpha_1) = 0\cdot70926$ Å, $\mu = 1\cdot01$ mm^{-1}, $F(000) = 524$, $T = 297$ K, final $R = 0\cdot038$ for 3130 observed reflections. Two silver atoms are joined in dimeric pairs by bridging coordinating carboxyl groups from two pefloxacin molecules. The terminal piperazinyl N atom from another pefloxacin molecule also coordinates to each Ag atom. The silver coordination is completed by an O atom from a water molecule and, possibly, a bond to the other silver atom (Ag—Ag = 2·901 Å). Since both ends of the pefloxacin molecules are coordinated to silver, the dimeric silver pairs are linked into a chain extending through the crystal. The general features of the structure are strikingly similar to those of silver sulfadiazine, a well known burn treatment compound.

Introduction. The complex of a sulfa drug, sulfadiazine, with silver now appears to be one of the most effective agents for the control of infections in severely burned patients (Fox, 1968; Modak & Fox, 1973; Fox & Modak, 1974). Its crystal structure determination (Baenziger & Struss, 1976; Cook & Turner, 1975) showed that its low solubility is due to its polymeric nature in the crystal form. A few strains of bacteria have developed resistance to silver sulfadiazine, however, so that a search has continued for additional compounds which might be effective as topical burn treatment agents. Modak & Fox (1981) have discovered that a silver salt of 1-ethyl-6-fluoro-1,4-dihydro-4-oxo-7-(1-piperazinyl)-3-quinolinecarboxylic acid is very effective in controlling bacterial infections in burned mice and rats, including efficacy against strains of bacteria which have developed resistance to silver sulfadiazine. The crystal structure of a silver salt of a very closely related compound, 1-ethyl-6-fluoro-1,4-dihydro-7-(4-methyl-1-piperazinyl)-4-oxo-3-quinolinecarboxylic acid, pefloxacin (1), has been undertaken to discover if any structural relationship exists between these two complexes.



(1)
Pefloxacin



(2)
Nalidixic acid

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Experimental. A powdered preparation of the silver pefloxacin complex was dissolved in an aqueous ammonium hydroxide solution. Ammonia and excess water were removed slowly by placing a beaker of the ammoniacal solution and a beaker of concentrated sulfuric acid in a closed desiccator for several days, yielding clear colorless crystals. The crystals rapidly changed from clear to opaque when exposed to ambient low levels of water vapor in the air, presumably due to loss of water. For intensity data collection, a single crystal was sealed in a glass capillary together with a small amount of mother liquor. The crystal structure determination showed that the cell contained two units of Ag(pefloxacin).$4H_2O$. Air-dried samples analyzed for C, H, N corresponded to Ag(pefloxacin).$2H_2O$ (calc. for $AgFO_3N_3C_{17}H_{19}.2H_2O$ is C 42·87, N 8·82, H 4·86%; found C 42·55, N 8·79, H 4·94%). In the structure, not all water molecules are equivalently bound, so that it is not surprising that some loss of water occurs readily.

Single-crystal intensity data (8959 reflections, h, ±10; k, ±11; l, −14 to +15) obtained with a FACS diffractometer using a 2θ step-scan procedure (Baenziger, Foster, Howells, Howells, Vander Valk & Burton, 1977), basic step size of 0·20° was adjusted for dispersion; $2\theta_{\max} = 50°$. Averaging equivalent reflections gave 3621 unique reflections, 3130 greater than $3\,\sigma_{\rm bkg}$. Standard reflections, 063, 006 and 402, measured every 60 reflections varied by 2·3, 1·8 and 8·0%. Data were corrected for absorption; crystal bounding faces and distances between faces in mm: ±(001), 0·027, ±(111), 0·358; ±(021), 0·79; absorption corrections, 1·03 to 1·26 (Templeton & Templeton, 1973). After standard and absorption corrections (the variation of standard 402 was ignored in making standard corrections) the average agreement among equivalent reflections, 3·7%, indicated no serious decomposition problems. The crystal changed from colorless to deep amber during the course of data collection. Cell dimensions obtained from 12 reflections in angular range 40–50° 2θ. Structure solved by Patterson method and electron density map methods. $R = 0·09$ with only isotropic non-hydrogen atoms; $R = 0·05$ with anisotropic non-hydrogen atoms; $R = 0·041$ with anisotropic non-hydrogen atoms and all H atoms except the water molecules; $R = 0·038$ including all atoms ($wR = 0·058$). All H atoms, except those on the water molecules, were located from the difference map when $R = 0·05$, and the H atoms were located on the water molecules in the difference map at $R = 0·041$. Except for the water molecules, the H-atom positions were adjusted a minor amount to make their C—H distance equal to 0·95 Å. The direction of the O—H bond in the water molecules was maintained at fixed orientations during subsequent refinement. Atomic scattering factors for Ag, F, O, N, C from *International Tables for X-ray Crystallography* (1974); for H from Stewart, Davidson & Simpson (1965). Weights used in refinement minimizing $\sum w(F_o - F_c)^2$ were those estimated from counting statistics $\sigma(F^2)$ corrected by an ignorance factor, $p = 0·06$ where $w = 1/\sigma^2$, $\sigma = [\sigma^2(F^2) + p^2F_o^{\,4}]^{1/2}/2F_o$. Parameter shifts were less than 0·12 times the e.s.d. in the last cycle of least squares. The residual density in the final difference electron density map was 1·0 e Å^{-3} in the vicinity of the silver atom and less than 0·4 e Å^{-3} in the remainder of the map. Computer programs used were local adaptations of programs from Lawrence Radiation Laboratory, Berkeley, for least squares and electron density maps.

Table 1. *Positional parameters in the title compound*

	x	*y*	*z*
Ag	0·34286 (3)	0·02145 (2)	0·08033 (2)
N(1)	0·6244 (4)	−0·4504 (3)	0·5633 (3)
C(2)	0·6093 (4)	−0·5647 (3)	0·6569 (3)
C(3)	0·4794 (5)	−0·5939 (3)	0·7553 (3)
C(4)	0·3494 (4)	−0·4954 (4)	0·7687 (3)
O(4)	0·2305 (3)	−0·5058 (3)	0·8587 (2)
C(5)	0·2423 (4)	−0·2687 (4)	0·6693 (3)
C(6)	0·2575 (5)	−0·1537 (4)	0·5739 (3)
F(6)	0·1461 (3)	−0·0488 (3)	0·5837 (2)
C(7)	0·3870 (4)	−0·1332 (3)	0·4703 (3)
C(8)	0·5084 (4)	−0·2343 (3)	0·4677 (3)
C(9)	0·4992 (4)	−0·3518 (3)	0·5654 (3)
C(10)	0·3649 (4)	−0·3721 (3)	0·6669 (3)
C(11)	0·4812 (4)	−0·7340 (3)	0·8467 (3)
O(12)	0·3452 (3)	−0·8014 (3)	0·9147 (2)
O(13)	0·6226 (3)	−0·7792 (3)	0·8470 (3)
C(*E*1)	0·7788 (5)	−0·4265 (4)	0·4628 (3)
C(*E*2)	0·8973 (5)	−0·3179 (5)	0·4532 (4)
N(*P*1)	0·3934 (4)	−0·0141 (3)	0·3766 (3)
C(*P*2)	0·5404 (4)	0·0070 (4)	0·2746 (3)
C(*P*3)	0·5478 (5)	0·1551 (4)	0·1885 (3)
N(*P*4)	0·3954 (4)	0·1824 (3)	0·1637 (3)
C(*P*5)	0·2529 (5)	0·1642 (4)	0·2683 (4)
C(*P*6)	0·2420 (5)	0·0136 (4)	0·3503 (3)
C(*M*)	0·4059 (7)	0·3320 (4)	0·0867 (4)
O(*W*1)	0·0409 (4)	0·0455 (4)	0·1516 (4)
O(*W*2)	0·1442 (4)	−0·8000 (3)	0·7963 (3)
O(*W*3)	0·0443 (5)	−0·3187 (4)	0·9763 (4)
O(*W*4)	0·1103 (5)	−0·3963 (4)	0·1943 (5)

The atomic parameters are listed in Table 1. Interatomic distances are listed in Table 2.*

Discussion. A view of the complex structure, minus the non-coordinated water molecules, is shown in Fig. 1. The pefloxacin molecule is coordinated to Ag atoms at both ends of the molecule. Two Ag atoms are linked together by two carboxyl groups from two pefloxacin molecules, each carboxyl group bridging between the two Ag atoms [Ag—O(12) = 2·329 (3), Ag—O(13) = 2·285 (3) Å]. A third coordination site on each Ag

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* Lists of temperature factor parameters, a table of calculated and observed structure factors, equations of least-squares planes, hydrogen parameters and additional atomic distance values including those involving hydrogen atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43111 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

atom is occupied by the terminal nitrogen atom, N(*P*4), of the piperazine ring of another molecule [Ag—N(*P*4) = 2·431 (3) Å]. A fourth coordination site is occupied by the O atom of a water molecule [Ag—O(*W*1) = 2·454 (4) Å]. The two linked Ag atoms are just 2·901 (1) Å from each other, so that a fifth coordination site can be considered to be filled by the other Ag atom. Alternatively, one could consider that instead of distorted trigonal bipyramidal coordination about Ag, the coordination is distorted tetrahedral, with the close Ag—Ag distance being an accidental result of the linking coordination of the carboxyl group. (Under this latter alternative, there appears to be no reason that the two Ag atoms be so close to one another.) This coordination about the Ag atom is strikingly similar to that in silver sulfadiazine (Baenziger & Struss, 1976) (the comparable bond angles are given in Table 2), so that a four-center bonding system in the apical direction of the distorted trigonal bipyramid may also be operating here.

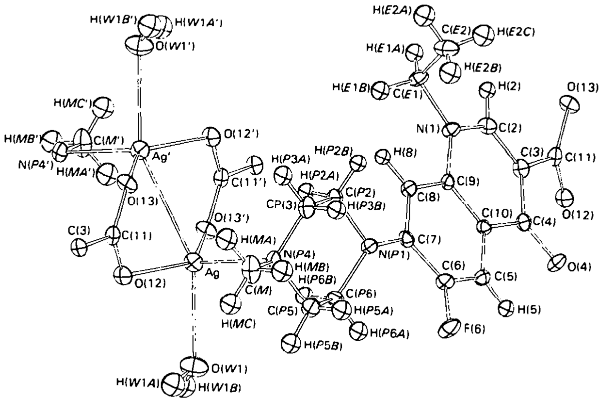

Fig. 1. Structure of silver pefloxacin, showing atomic numbering.

Table 2. *Interatomic bond distances* (Å) *and angles* (°) *for the title compound; e.s.d.'s in parentheses*

Silver coordination	
Ag—Ag	2·901 (1)
Ag—O(*W*1)	2·454 (4)
Ag—O(12)	2·329 (3)
Ag—N(*P*4)	2·431 (3)
Ag—O(13)	2·285 (3)
Piperazinyl group	
N(*P*1)—C(*P*2)	1·460 (5)
N(*P*1)—C(*P*6)	1·475 (5)
C(*P*2)—C(*P*3)	1·511 (5)
C(*P*3)—N(*P*4)	1·473 (5)
N(*P*4)—C(*P*5)	1·465 (6)
N(*P*4)—C(*M*)	1·469 (4)
C(*P*5)—C(*P*6)	1·501 (5)

	Pefloxacin molecule	Nalidixic acid*
N(1)—C(9)	1·393 (4)	1·387 (9)
N(1)—C(2)	1·351 (5)	1·316 (9)
N(1)—C(*E*1)	1·480 (5)	1·478 (10)
C(2)—C(3)	1·348 (6)	1·384 (11)
C(3)—C(4)	1·424 (5)	1·436 (10)
C(3)—C(11)	1·510 (4)	1·461 (9)
C(11)—O(12)	1·258 (5)	1·323 (9)
C(11)—O(13)	1·272 (5)	1·230 (10)
C(4)—C(10)	1·466 (5)	1·445 (9)
C(4)—O(4)	1·254 (5)	1·261 (8)
C(10)—C(5)	1·407 (5)	1·418 (10)
C(10)—C(9)	1·402 (5)	1·407 (9)
C(5)—C(6)	1·370 (5)	1·361 (10)
C(6)—C(7)	1·401 (6)	1·406 (11)
C(6)—F(6)	1·360 (4)	—
C(7)—C(8)	1·386 (5)	C—N, 1·325 (9)
C(7)—N(*P*1)	1·392 (5)	C—C, 1·522 (11)
C(8)—C(9)	1·412 (5)	C—N, 1·353 (8)

Ethyl group

C(*E*1)—C(*E*2) 1·496 [1·490 (11) in nalidixic acid]

Hydrogen-bond distances	
O(*W*1)—H(*W*1*B*)···O(*W*2)	2·758 (5)
O(*W*1)—H(*W*1*A*)···O(*W*3)	2·864 (6)
O(*W*2)—H(*W*2*A*)···O(12)	2·812 (4)
O(*W*2)—H(*W*2*B*)···O(*W*4)	2·804 (5)
O(*W*3)—H(*W*3*A*)···O(4)	2·874 (5)
O(*W*3)—H(*W*3*B*)···O(4)′	2·779 (5)
O(*W*4)—H(*W*4*B*)···O(13)	2·790 (6)

Pefloxacin molecule		Corresponding angles in Ag sulfadiazine†	
Ag—Ag—O(12)	78·17 (7)	Ag—Ag—N(5)	69·8 (1)
Ag—Ag—N(*P*4)	108·22 (8)	Ag—Ag—O(3)	88·4 (1)
Ag—Ag—O(13)	76·67 (8)	Ag—Ag—N(11)	84·1 (2)
O(12)—Ag—N(*P*4)	97·4 (1)	N(5)—Ag—O(3)	84·1 (2)
N(*P*4)—Ag—O(13)	118·8 (2)	O(3)—Ag—N(11)	129·3 (2)
O(13)—Ag—O(12)	140·8 (2)	N(11)—Ag—N(5)	137·6 (2)
O(*W*1)—Ag—O(12)	85·9 (1)	N(7)—Ag—N(5)	99·3 (2)
O(*W*1)—Ag—O(13)	104·8 (1)	N(7)—Ag—N(11)	113·7 (2)
O(*W*1)—Ag—N(*P*4)	93·8 (2)	N(7)—Ag—O(3)	73·7 (2)
O(*W*1)—Ag—Ag	154·2 (1)	N(7)—Ag—Ag	160·2 (2)

Carboxyl group	Pefloxacin molecule	Nalidixic acid
C(3)—C(11)—O(12)	118·7 (3)	116·7 (7)
C(3)—C(11)—O(13)	117·2 (3)	124·0 (7)
O(12)—C(11)—O(13)	124·1 (3)	119·3 (6)
Ethyl group		
N(1)—C(*E*1)—C(*E*2)	111·9 (4)	112·7 (6)

Piperazinyl group			
C(7)—N(*P*1)—C(*P*2)	117·3 (3)	C(*P*3)—N(*P*4)—C(*P*5)	108·6 (4)
C(7)—N(*P*1)—C(*P*6)	117·3 (3)	C(*P*3)—N(*P*4)—C(*M*)	109·1 (3)
C(*P*2)—N(*P*1)—C(*P*6)	110·3 (3)	C(*P*5)—N(*P*4)—C(*M*)	109·1 (3)
N(*P*1)—C(*P*2)—C(*P*3)	111·3 (3)	C(*P*3)—N(*P*4)—Ag	114·5 (2)
C(*P*2)—C(*P*3)—N(*P*4)	112·2 (3)	C(*P*5)—N(*P*4)—Ag	107·4 (2)
N(*P*4)—C(*P*5)—C(*P*6)	110·4 (3)	Ag—N(*P*4)—C(*M*)	108·0 (2)
C(*P*5)—C(*P*6)—N(*P*1)	110·3 (3)		

	Pefloxacin molecule	Nalidixic acid
C(9)—N(1)—C(2)	119·3 (3)	119·7 (6)
C(*E*1)—N(1)—C(9)	121·1 (3)	120·7 (5)
C(*E*1)—N(1)—C(2)	119·4 (3)	119·6 (6)
N(1)—C(2)—C(3)	125·1 (3)	125·3 (7)
C(11)—C(3)—C(4)	123·5 (3)	121·0 (6)
C(11)—C(3)—C(2)	116·4 (3)	120·2 (6)
C(2)—C(3)—C(4)	120·1 (3)	118·8 (8)
O(4)—C(4)—C(3)	125·4 (3)	122·9 (6)
O(4)—C(4)—C(10)	120·0 (3)	121·9 (6)
C(3)—C(4)—C(10)	114·6 (3)	115·2 (6)
C(4)—C(10)—C(5)	119·8 (3)	121·9 (6)
C(9)—C(10)—C(5)	117·8 (3)	116·1 (6)
C(9)—C(10)—C(4)	122·3 (3)	122·0 (6)
C(10)—C(5)—C(6)	119·5 (4)	119·7 (7)
C(5)—C(6)—C(7)	124·0 (3)	119·4 (7)
C(5)—C(6)—F(6)	117·0 (3)	—
F(6)—C(6)—C(7)	118·8 (3)	—
C(6)—C(7)—N(*P*1)	120·7 (3)	C—C—C, 120·3 (7)
C(6)—C(7)—C(8)	116·6 (4)	C—C—N, 123·2 (7)
N(*P*1)—C(7)—C(8)	122·6 (3)	C—C—N, 116·4 (7)
C(7)—C(8)—C(9)	120·8 (3)	C—N—C, 117·1 (6)
C(8)—C(9)—C(10)	121·1 (3)	N—C—C, 124·5 (6)
C(8)—C(9)—N(1)	120·6 (3)	N—C—N, 116·6 (6)
C(10)—C(9)—N(1)	118·2 (3)	118·9 (5)

* Achari & Neidle (1976).

† Baenziger & Struss (1976).

The net result of the ligand molecule's being coordinated at both ends, and the carboxyl groups' bridging between two Ag atoms is the creation of a double-chained connection of Ag atom pairs which extends throughout the crystal. Again, the general features of this chain are similar to those found in silver sulfadiazine.

The pefloxacin molecule. The bond distances in the pefloxacin molecule appear to correspond reasonably well to the distances found in other molecules of this type, and some of the comparable distances found in nalidixic acid (2) (Achari & Neidle, 1976) [1-ethyl-1-4-dihydro-7-methyl-1,8-naphthyridin-4-one-3-carboxylic acid] are listed in Table 2. The C—O distances, 1·254, 1·258, 1·272 Å, are only slightly longer than those expected for ketone or carboxyl groups. The C(2)—C(3) bond distance [1·348 (6) Å] is shortened to that of a double bond, in keeping with the quinonic nature of that ring; the C(3)—C(4) [1·424 (5) Å] and C(4)—C(10) [1·466 (5) Å] distances are also in keeping with the less aromatic character of this ring. In contrast, as in nalidixic acid, the distances in the other ring [C(5), C(6), C(7), C(8), C(9), C(10): 1·407, 1·370, 1·401, 1·386, 1·412, 1·402 (all ±0·005) Å] are closer to the aromatic norm. Reflecting their more aromatic character, the C—N distances of N(1)—N(2) [1·351 (5)], N(1)—C(9) [1·393 (4)], and C(7)—N(*P*1) [1·392 (5) Å] are all shorter than those of the aliphatic piperazinyl ring [1·460, 1·475, 1·473, 1·465], N(*P*4)—C(*M*) [1·469] and N(1)—C(*E*1) [1·480 Å] (all ±0·005 Å) values. The aliphatic C—C distances from the piperazinyl ring and the ethyl group, 1·511, 1·501 and 1·496 Å, are all somewhat shorter than the idealized C—C single-bond distance, but no bond-distance corrections have been made here for the thermal motion of the atoms.

The molecule is oriented in Fig. 2 so that one is looking approximately at the edge of the planar quinoline ring (planarity of the various groups is shown in the deposited Table 5). From this view one can clearly see the twist of the carboxyl group out of the plane of the quinoline ring. The twist of about 35° is undoubtedly due to repulsion by the oxo O(4) atom, since even after the twist and the opening of the C(4)—C(3)—C(11) angle to 123°, the O—O distance is 2·93 Å. In nalidixic acid, the H atom in the carboxyl group is hydrogen-bonded to the oxo O(4) atom, so that the carboxyl group remains more nearly planar. Fig. 2 also displays the chair form of the piperazine ring, and the out-of-plane orientation of the ethyl group attached to N(1). The orientations of the ethyl group in nalidixic acid and in pefloxacin are virtually identical.

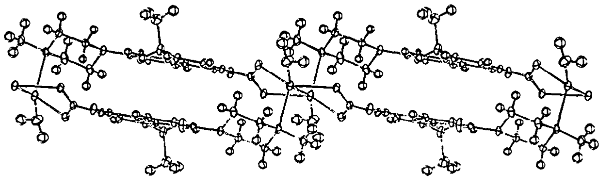

Fig. 2. View of the molecule looking approximately in the plane of the quinoline ring. The twist of the carboxyl group out of this plane is clearly shown.

Possible O—H···O hydrogen bonds were identified from the O···O distances in the neighborhood of 2·7 to 2·8 Å. Electron density difference maps clearly showed the presence of H atoms along some of these O···O contacts and not along others. (As noted earlier, the H-atom positions were not refined, and since the ability to locate H atoms is near the resolution of the data, no particular reliance should be placed on the O—H and H···O distances or on the bond angles found.) They all appear to be very tetrahedrally oriented about O atoms, with only slight to moderately bent hydrogen bonds. Perhaps the most important feature is the difference in binding of the water molecules. O(*W*1) is bonded to Ag, and both H atoms are involved in hydrogen bonds [to O(*W*2) and to O(*W*3)]. O(*W*2) has both H atoms involved in hydrogen bonding [to O(12) and O(*W*4)], and it is a recipient of a hydrogen bond from O(*W*1). O(*W*3) also has both H atoms involved in hydrogen bonding to two different O(4) atoms, and receives a hydrogen bond from O(*W*1). O(*W*4) has only one H atom involved in hydrogen bonding [to O(13)], and it receives a hydrogen bond from O(*W*2). O(*W*4) also has the largest temperature factors of the four solvent molecules, and it is likely that it is the solvent molecule which is most readily lost when the crystal decomposes in dry air.

The relationship between the structures of silver sulfadiazine and silver pefloxacin and their effectiveness in controlling bacterial infections in burns is not clear at this time. The similarity of the general features of their structures, however, has prompted a further investigation of some closely related materials, some of which are effective and some of which are relatively ineffective therapeutic agents.

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Single-Strand Polymer in *catena*-Poly{[*trans*-bis(6,8-dimethyl[1,2,4]triazolo[3,4-*b*]pyridazine-N^2)cadmium]-μ-(thiocyanato-*N:S*)-μ-(thiocyanato-*S:N*)}

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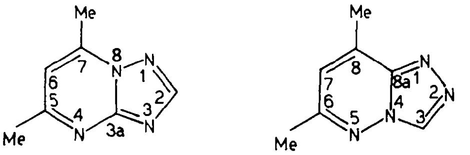
Abstract. $[Cd(C_7H_8N_4)_2(NCS)_2]_n$, $M_r = 524{\cdot}90$ (monomeric unit), monoclinic, $P2_1/c$, $a = 19{\cdot}560\,(5)$, $b = 9{\cdot}562\,(4)$, $c = 11{\cdot}521\,(4)$ Å, $\beta = 94{\cdot}25\,(1)°$, $V = 2149\,(1)$ Å^3, $Z = 4$, D_m(by flotation) = 1·62 (1), $D_x = 1{\cdot}62$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54178$ Å, $\mu = 10{\cdot}361$ mm^{-1}, $F(000) = 1048$, room temperature, $R = 0{\cdot}041$ for 2224 independent observed reflections. The Cd$^{\mathrm{II}}$ cation is octahedrally coordinated by two monodentate N-bonded organic ligands (*trans*) with Cd—N bonds of 2·396 (8) and 2·357 (8) Å, two N-bonded thiocyanate groups (*cis*) with Cd—N distances of 2·311 (8) and 2·347 (9) Å and two S-bonded thiocyanate groups (*cis*) with Cd—S bonds of 2·783 (3) and 2·680 (3) Å. The double thiocyanate bridge links the Cd$^{\mathrm{II}}$ cations to form slightly zigzag polymeric chains running along **c**.

Introduction. Organic bases differing from purine derivatives in the position and/or number of ring nitrogen atoms (azapurines) are known to form complexes with transition metals (Dillen, Lenstra, Haasnoot & Reedijk, 1983; Biagini Cingi, Manotti Lanfredi, Tiripicchio, Haasnoot & Reedijk, 1983). Therefore, they may be used as model compounds for the study of the interactions of these metals with nucleic bases and their derivatives. The non-hydrazinic triazole-ring nitrogen atom [N(3)] of 5,7-dimethyl[1,2,4]-triazolo[1,5-*a*]pyrimidine (dmtp) (see scheme) has been shown to be preferred for coordination from several structural determinations of its metal complexes (Biagini Cingi, Manotti Lanfredi, Tiripicchio, Haasnoot & Reedijk, 1984, 1985; Biagini Cingi, Manotti Lanfredi, Tiripicchio, Reedijk & Haasnoot, 1986). As was pointed out earlier (Biagini Cingi, Manotti Lanfredi, Tiripicchio, Haasnoot & Reedijk, 1984) this preference may be due to the presence of adjacent bulky substituents in the ring.

We have now investigated the behaviour as a ligand of 6,8-dimethyl[1,2,4]triazolo[3,4-*b*]pyridazine (hereafter abbreviated as dmtpz). In this ligand only hydrazinic nitrogen atoms are available for coordination, two in the triazole ring, one in the pyridazine ring. Steric arguments would predict coordination at N(2) of dmtpz.



dmtp dmtpz

IUPAC numbering schemes of dmtp and dmtpz ligands.

Crystals of the thiocyanate complex Cd(dmtpz)$_2$-(NCS)$_2$ were obtained from aqueous solutions. Their X-ray structure was solved in order to compare it with that of the cadmium thiocyanate complex of the isomeric ligand dmtp, Cd(dmtp)$_2$(NCS)$_2$(H$_2$O)$_2$ (Dillen, Lenstra, Haasnoot & Reedijk, 1983).

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