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Tetrakis(1-methyl-4-imidazoline-2-thione)platinum(II) Dichloride Dihydrate

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Abstract. Yellow crystals of [Pt(C₄H₆N₂S)₄]Cl₂·2H₂O, C₁₆H₂₄N₈PtS₄²⁺·2Cl⁻·2H₂O, were prepared from K₂PtCl₄ and 1-methyl-2-imidazoethiol in a 1:1 water-methanol solution. Space group *P*1̄, *a* = 8.774 (2), *b* = 9.830 (2), *c* = 10.430 (3) Å, *α* = 107.07 (2), *β* = 125.84 (2), *γ* = 92.90 (2)°, *D*_m = 1.88 (1), *D*_c = 1.88 g cm⁻³ for *Z* = 1. The Pt atom lies at an inversion centre and is planar coordinated by four S atoms. Each chloride counter ion is linked by four hydrogen bonds to two N–H groups of [Pt(C₄H₆N₂S)₄]²⁺ ions and two H₂O molecules of crystallization. Each H₂O molecule forms a bridge between two chloride ions, thus forming a continuous hydrogen-bonded structure. The final *R* value is 0.0176 for 3875 independent reflections.

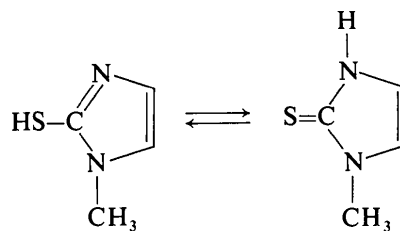
Introduction. The title compound was prepared in order to obtain information on the coordinating behaviour of the potentially ambidentate ligand 1-methyl-2-imidazoethiol with heavy metals such as

platinum. This ligand can bind through the heterocyclic N atom, or through the exocyclic S atom (Cavalca, Damiano, Musatti & Sgarabotto, 1968; Battaglia, Corradi, Nardelli & Tani, 1976; Raper & Nowell, 1979; Nowell, Cox & Raper, 1979), and even through both N and S atoms when the ligand is deprotonated (Agnus, Louis & Weiss, 1980). Infrared data (Jordanov, 1978) indicate the ligand to be monodentate in the title compound, and water molecules also to be present (sharp bands at 3500 and 3436 cm⁻¹). The detailed coordination geometry around the Pt atom could not, however, be established solely from the spectroscopic data. The present structural study has therefore been undertaken. The quality of the crystals appeared to be extremely good. The intensities of 3875 independent reflections were measured on a Nonius CAD4 automatic diffractometer using a crystal of 0.35 × 0.27 × 0.26 mm [graphite-monochromated Mo *K*α radiation, λ(*α*₁) = 0.70930 Å, θ < 28°]. No less than 3853 of these satisfied the criterion *I* > 2σ(*I*).

Intensity-control reflections measured at regular intervals indicated a decrease in intensity of 3% during the data collection. Lorentz, polarization, absorption, extinction and decomposition corrections were applied ($\mu = 58.4 \text{ cm}^{-1}$). All 3875 independent reflections were used for the solution and refinement of the structure. The choice of the space group *P*1 was justified by the successful refinement of the structure. Atomic scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974). The structure was solved by the direct-methods program *MULTAN* (Main, Woolfson & Germain, 1978), full-matrix least-squares refinements and Fourier syntheses. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = (1/\sigma_{\text{stat}}^2)$. All hydrogen atoms were located in difference Fourier maps. Refinement of all atomic positional parameters together with anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms resulted in final residuals of $R = 0.0176$ and $R_w = 0.0186$. A final

difference Fourier synthesis showed no excursions above background. The atomic positional and thermal parameters are listed in Table 1.*

Discussion. The Pt atom in the structure lies at an inversion centre and has a square-planar coordination involving the four ligand S atoms (Fig. 1). The ligand is present in its thione tautomeric form:



1-methyl-2-imidazoethiol

1-methyl-4-imidazoline-2-thione

Table 1. Atomic fractional positional parameters ($\times 10^4$, for H $\times 10^3$)

The hydrogen atoms are labelled with the names of the atoms to which they are bonded. For explanation of atomic labels see Fig. 1.

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}^*/B_{\text{iso}}^\dagger$ (\AA^2)
Pt	5000	5000	5000	1.80 (1)
Cl	4816 (1)	7253 (1)	8692 (1)	3.97 (3)
S(A)	4944 (1)	7040 (1)	4305 (1)	3.03 (2)
N(1A)	7494 (3)	9819 (2)	6361 (3)	2.95 (8)
N(2A)	6744 (3)	8958 (2)	7653 (3)	2.97 (8)
C(1A)	6456 (3)	8617 (2)	6170 (3)	2.49 (8)
C(2A)	7966 (5)	10380 (3)	8783 (4)	3.86 (1)
C(3A)	8426 (5)	10915 (3)	7982 (4)	3.97 (2)
C(4A)	7653 (6)	9952 (4)	5086 (5)	4.15 (6)
S(B)	1689 (1)	4014 (1)	2611 (1)	2.77 (2)
N(1B)	-1193 (2)	5318 (2)	1959 (2)	2.55 (7)
N(2B)	1171 (2)	6064 (2)	4676 (2)	2.63 (7)
C(1B)	567 (2)	5177 (2)	3123 (3)	2.15 (7)
C(2B)	-236 (3)	6753 (3)	4496 (4)	3.32 (0)
C(3B)	-1700 (3)	6286 (3)	2814 (4)	3.45 (1)
C(4B)	-2429 (3)	4501 (3)	91 (3)	3.44 (0)
O	2307 (5)	9676 (4)	8013 (4)	7.06 (3)
H(N2A)	610 (5)	837 (4)	781 (4)	5.3 (8)
H(C2A)	834 (4)	1077 (3)	985 (4)	4.4 (7)
H(C3A)	917 (5)	1179 (4)	828 (4)	4.9 (7)
H(C4A1)	729 (6)	1078 (5)	486 (5)	8.1 (11)
H(C4A2)	894 (6)	1000 (4)	544 (5)	6.7 (9)
H(C4A3)	686 (7)	921 (5)	409 (6)	8.5 (3)
H(N2B)	236 (4)	617 (3)	570 (4)	3.3 (6)
H(C2B)	-3 (4)	745 (3)	540 (4)	4.0 (6)
H(C3B)	-282 (5)	655 (4)	219 (4)	4.6 (7)
H(C4B1)	-310 (5)	351 (4)	-26 (4)	5.0 (7)
H(C4B2)	-323 (5)	514 (4)	-42 (4)	6.3 (9)
H(C4B3)	-170 (5)	474 (4)	-11 (5)	6.2 (10)
H(1O)	308 (7)	1047 (5)	874 (6)	8.5 (13)
H(2O)	297 (7)	903 (6)	826 (6)	9.7 (15)

* $B_{\text{eq}} = \frac{2}{3}\pi^2 \text{ trace } \bar{U}$.

† The temperature factor is of the form $\exp(-B_{\text{iso}} \sin^2 \theta/\lambda^2)$.

Bond lengths and angles are given in Table 2. The C=S distances of 1.716 (2) and 1.712 (2) \AA in the present compound are not significantly different from the C=S double-bond lengths of 1.71 (2) and 1.72 (2) \AA in bis(ethylenethiourea)gold(I) chloride (Jones, Guy & Sheldrick, 1976). A further comparison of these two structures shows also that the Pt-S-C angles of 109.19 (7) and 104.55 (7) $^\circ$ are similar to the Au-S-C angles [111.2 (7) and 109.8 (1) $^\circ$] in the thiourea derivative. The thione form of the present ligand has also been found in e.g. distorted tetrahedral [Co(C₄H₆N₂S)₄](ClO₄)₂ with a C=S bond of 1.717 (4) \AA and a Co-S-C angle of 104.2 $^\circ$ (Raper &

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36793 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

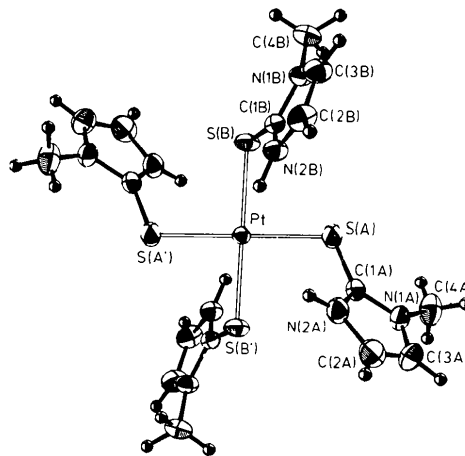


Fig. 1. The Pt(C₄H₆N₂S)₄²⁺ ion showing the atomic labelling and the thermal vibration ellipsoids (probability 50%). The hydrogen atoms are represented by small spheres.

Table 2. Bond lengths (Å) and angles (°)

Symmetry code: (i) 1 - x, 1 - y, 1 - z.

Pt-S(A)	2.3173 (5)	Pt-S(B)	2.3254 (5)
S(A)-C(1A)	1.716 (2)	S(B)-C(1B)	1.712 (2)
N(1A)-C(3A)	1.382 (3)	N(1B)-C(3B)	1.381 (3)
N(1A)-C(4A)	1.458 (4)	N(1B)-C(4B)	1.461 (3)
N(2A)-C(2A)	1.377 (3)	N(2B)-C(2B)	1.381 (3)
N(2A)-H(N2A)	0.90 (3)	N(2B)-H(N2B)	0.92 (3)
C(1A)-N(1A)	1.344 (3)	C(1B)-N(1B)	1.343 (2)
C(1A)-N(2A)	1.340 (3)	C(1B)-N(2B)	1.336 (3)
C(2A)-C(3A)	1.329 (4)	C(2B)-C(3B)	1.339 (3)
C(2A)-H(C2A)	0.90 (3)	C(2B)-H(C2B)	0.90 (30)
C(3A)-H(C3A)	0.90 (3)	C(3B)-H(C3B)	0.92 (3)
C(4A)-H(C4A1)	0.93 (4)	C(4B)-H(C4B1)	0.95 (3)
C(4A)-H(C4A2)	0.95 (4)	C(4B)-H(C4B2)	0.99 (4)
C(4A)-H(C4A3)	0.87 (4)	C(4B)-H(C4B3)	0.82 (4)
O-H(1O)	0.80 (5)	O-H(2O)	0.88 (5)
S(A)-Pt-S(B)	87.31 (2)	S(A)-Pt-S(B)	92.69 (2)
Pt-S(A)-C(1A)	109.19 (7)	Pt-S(B)-C(1B)	104.55 (7)
C(1A)-N(1A)-C(3A)	109.2 (2)	C(1B)-N(1B)-C(3B)	109.1 (2)
C(1A)-N(1A)-C(4A)	125.9 (2)	C(1B)-N(1B)-C(4B)	125.3 (2)
C(3A)-N(1A)-C(4A)	124.9 (2)	C(3B)-N(1B)-C(4B)	125.5 (2)
C(1A)-N(2A)-C(2A)	110.0 (2)	C(1B)-N(2B)-C(2B)	109.8 (2)
S(A)-C(1A)-N(1A)	124.9 (2)	S(B)-C(1B)-N(1B)	124.3 (2)
S(A)-C(1A)-N(2A)	128.6 (2)	S(B)-C(1B)-N(2B)	129.1 (2)
N(1A)-C(1A)-N(2A)	106.3 (2)	N(1B)-C(1B)-N(2B)	106.6 (2)
N(2A)-C(2A)-C(3A)	106.9 (2)	N(2B)-C(2B)-C(3B)	106.9 (2)
C(2A)-C(3A)-N(1A)	107.6 (2)	C(2B)-C(3B)-N(1B)	107.6 (2)
H(1O)-O-H(2O)	105 (4)		

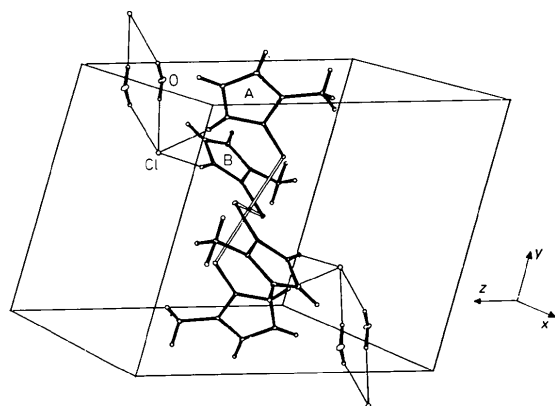


Fig. 2. The unit cell of Pt(C₄H₆N₂S)₄Cl₂·2H₂O. Hydrogen bonds are drawn as thin lines. The positions of the ligands A and B and of the Cl and O atoms as given in Table 1 are indicated.

Nowell, 1979). The crystal structure of the related free ligand 2-benzimidazolinethione shows that even there the thione form is the preferred tautomer (Form, Raper & Downie, 1976), having a C=S bond of 1.671 (8) Å.

Fig. 2 shows the unit cell of the title compound and the hydrogen bonding in the structure. The hydrogen-bond lengths are given in Table 3. The water molecules in the structure form hydrogen bonds to two chloride ions. Each chloride ion forms bridges between two water molecules and two independent N-H groups of different ligands. The packing of the molecules seems to

Table 3. Hydrogen bonds

Symmetry code: (ii) 1 - x, 2 - y, 2 - z.

A...H-D	A...D (Å)	A...H (Å)	∠A...H-D (°)
Cl-H(2O)-O	3.273 (3)	2.40 (5)	173 (5)
Cl-H(1O ⁱⁱ)-O ⁱⁱ	3.206 (3)	2.42 (5)	166 (5)
Cl-H(N2A)-N(2A)	3.126 (2)	2.24 (3)	170 (2)
Cl-H(N2B)-N(2B)	3.193 (2)	2.34 (3)	154 (2)

be very efficient. No disorder could be detected and even the CH₃ groups appear to have only a single, well-defined orientation.

JJ thanks Johnson and Matthey for a generous loan of K₂PtCl₄.

Note added in proof: After the present paper had been accepted for publication, another article appeared, describing the characterization and structure determination of the title compound, resulting in essentially the same structure (O'Neill, Raper, Daniels & Nowell, 1982). We claim that our structure is rather more accurate ($R = 0.0176$ vs. $R = 0.0958$; more accurate hydrogen-bonding information), and that the densities published by O'Neill *et al.* are wrong.

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