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$[Hg(pyridine)_2][Cr_2O_7]$, a compound used for a quick assay method to quantify soluble Hg^{II} ions

Matthias Weil

Institut für Mineralogie, Kristallographie und Strukturchemie der Technischen Universität Wien, Getreidemarkt 9/171, A-1060 Wien, Austria

Correspondence e-mail: mweil@mail.zserv.tuwien.ac.at

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
R factor = 0.018
wR factor = 0.046
Data-to-parameter ratio = 18.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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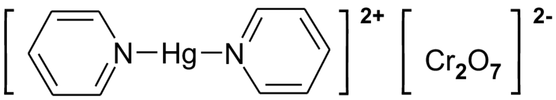
The title compound, bis(pyridine-N)mercury(II) dichromate(VI), $[Hg(C_5H_5N)_2][Cr_2O_7]$, is the first structurally determined representative of metal dichromates with additional pyridine ligands of general formula $[M(py)_n]_mCr_2O_7$ (py = pyridine) and can be used for a quick assay method to quantify Hg^{II} ions in solution. Two distinct Hg atoms, both located on special positions with symmetry 2 and $\overline{1}$, respectively, are coordinated octahedrally by two axial N atoms of pyridine rings at short distances $\overline{d}$(Hg—N) = 2.101 Å and four equatorial O atoms of dichromate groups at longer distances $\overline{d}$(Hg—O) = 2.620 Å. The dichromate group has a skew conformation with a bridging angle of 138.62 (17)°.

Comment

The preparation of metal dichromates(VI) with additional pyridine ligands (py) of general formula $[M(py)_n]_mCr_2O_7$ (n = 4, m = 1: M^{II} = Cu, Ni, Co, Zn, Cd, Mn; n = 3, m = 2: M^I = Ag; n = 2, m = 2: M^I = Ag; n = 2, m = 1: M^{II} = Hg) was described nearly 100 years ago (Briggs, 1908), but no crystallographic or structural data of these compounds have been reported in the meantime. Since the mercury compound is of considerable interest for application as a quick assay method to quantify mercury(II) ions in solution (Spacu & Dick, 1929), a structure analysis seemed desirable.



(I)

The two crystallographically independent mercury atoms are located at special positions with site symmetry 2 for Hg1 (Fig. 1) and $\overline{1}$ for Hg2 (Fig. 2), respectively. Both have a distorted octahedral coordination with two short axial bonds to N atoms of pyridine rings, $\overline{d}$(Hg—N) = 2.101 Å, and four longer equatorial bonds to terminal O atoms of the dichromate groups, $\overline{d}$(Hg—O) = 2.620 Å.

The Cr_2O_7 group (Fig. 3) displays a skew conformation with a dihedral angle of −31.58 (16)° for O2—Cr1···Cr2—O6 and a (Cr1—O4—Cr2) bridging angle of 138.62 (17)°. The two distinct $[CrO_4]$ tetrahedra show three short bonds $\overline{d}(Cr—O)_t$ = 1.614 Å to the terminal O atoms and a long bond $\overline{d}(Cr—O)_b$ = 1.768 Å to the bridging atom O4. The observed bond lengths and the bridging angle are in a range typical for other structures with dichromate groups and agree with those generally observed for $[X_2O_7]^{2-}$ anions (X = P, Cr, As, V) in inorganic

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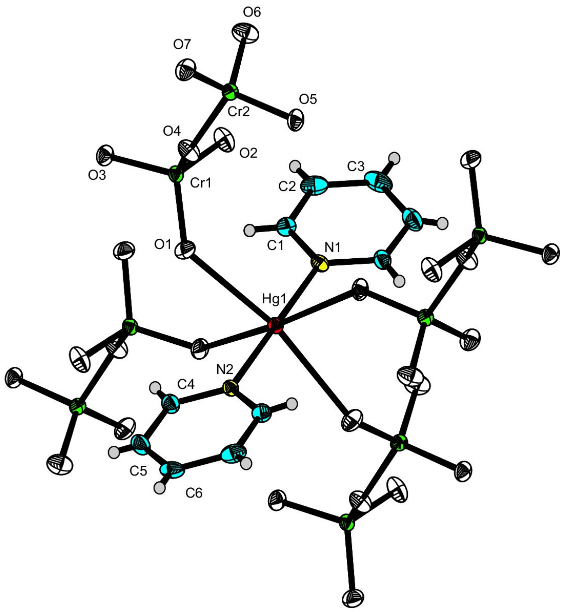

Figure 1
The coordination around Hg1, drawn with ellipsoids at the 25% probability level.

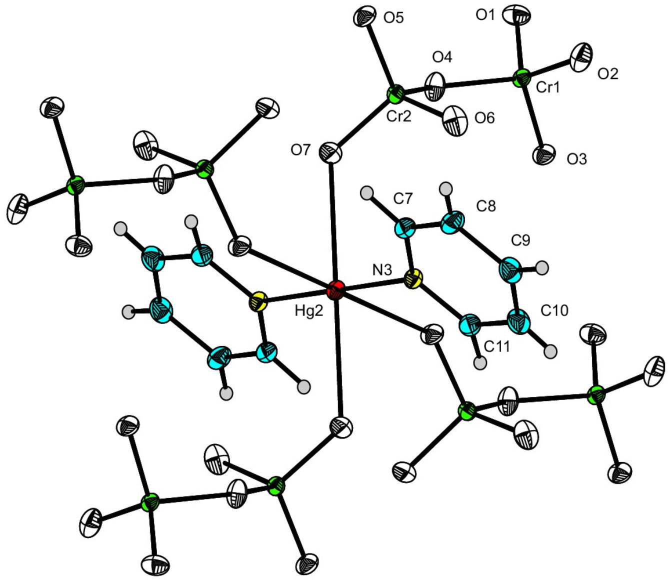

Figure 2
The coordination around Hg2, drawn with ellipsoids at the 25% probability level.

compounds (Brown & Calvo, 1970; Clark & Morley, 1976; Nord & Kierkegaard, 1980).

Single building units of $Hg(py)_2^{2+}$ and $Cr_2O_7^{2-}$ groups form layers parallel to the *ac* plane and extend along [101] (Fig. 4). The two-dimensional connection within a layer is achieved *via* bonding of different mercury atoms to shared dichromate groups, whereas no covalent bonding between two adjacent layers is evident. The junction between two parallel layers is mainly accomplished by van der Waals interactions. A further weak interaction between terminal O atoms of one layer and pyridine H atoms of adjacent layers with distances *d*(O2—H10) and *d*(O6—H2) of *ca* 2.30 Å leads to additional stabilization. Except for O2 and O6, which are exclusively bonded to Cr atoms, all other O atoms show coordination number 2.

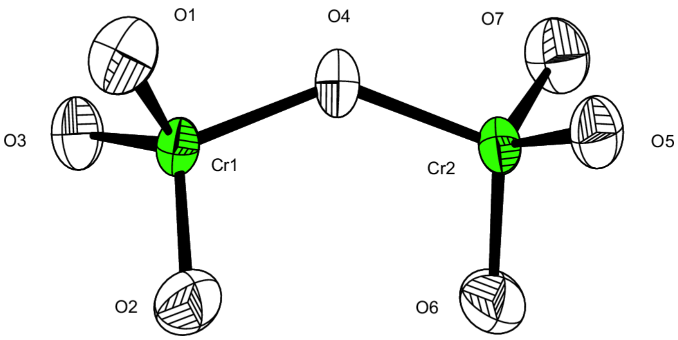

Figure 3
The dichromate group with skew conformation; ellipsoids are drawn at the 50% probability level.

Experimental

Microcrystalline $Hg(py)_2Cr_2O_7$ was prepared according to the method of Spacu & Dick (1929). Single crystals were grown by cooling an aqueous solution of the microcrystalline material, with two drops of pyridine added, from 393 K down to room temperature with a cooling rate of 2 K h^{-1}. The reaction was performed in a 5 ml Teflon-lined stainless steel container which was two-thirds filled. The orange crystals are light sensitive and blacken within a few days under normal daylight.

Crystal data

$[Hg(C_5H_5N)_2][Cr_2O_7]$
$M_r = 574.79$
Monoclinic, $C2/c$
$a = 15.4741$ (5) Å
$b = 15.0135$ (5) Å
$c = 14.0407$ (5) Å
$\beta = 115.018$ (1)°
$V = 2955.89$ (17) Å^3
$Z = 8$
$D_x = 2.583$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 10 078 reflections
$\theta = 2.7$–28.3°
$\mu = 11.84$ mm^{-1}
$T = 293$ (2) K
Parallelepiped, orange
0.10 × 0.07 × 0.04 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.366$, $T_{max} = 0.612$
19 668 measured reflections
3683 independent reflections
3186 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$
$\theta_{max} = 28.3°$
$h = -20 \rightarrow 20$
$k = -20 \rightarrow 20$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.018$
$wR(F^2) = 0.046$
$S = 1.21$
3683 reflections
204 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0166P)^2 + 2.3706P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.06$ e Å^{-3}
$\Delta\rho_{min} = -0.58$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.000071 (11)

Table 1

Selected geometric parameters (Å, °).

Hg1—N1	2.087 (4)	Hg2—O7	2.640 (3)
Hg1—N2	2.092 (4)	Cr1—O2	1.601 (3)
Hg1—O1	2.618 (3)	Cr1—O3	1.617 (3)
Hg1—O1^{i}	2.618 (3)	Cr1—O1	1.624 (3)
Hg1—O5^{ii}	2.625 (3)	Cr1—O4	1.766 (3)
Hg1—O5^{iii}	2.625 (3)	Cr1—Cr2	3.3075 (7)
Hg2—N3^{iv}	2.113 (3)	Cr2—O6	1.604 (3)
Hg2—N3	2.113 (3)	Cr2—O5	1.615 (3)
Hg2—O3^{v}	2.596 (3)	Cr2—O7	1.621 (3)
Hg2—O3^{vi}	2.596 (3)	Cr2—O4	1.769 (3)
Hg2—O7^{iv}	2.640 (3)		
Cr1—O4—Cr2	138.62 (17)		

Symmetry codes: (i) $-x, y, \frac{1}{2} - z$; (ii) $x - \frac{1}{2}, \frac{3}{2} - y, z - \frac{1}{2}$; (iii) $\frac{1}{2} - x, \frac{3}{2} - y, 1 - z$; (iv) $\frac{1}{2} - x, \frac{3}{2} - y, 2 - z$; (v) $-x, y, \frac{3}{2} - z$; (vi) $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$.

H atoms were located by difference Fourier maps and refined with a riding model.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ATOMS for Windows* (Dowty, 1998); software used to prepare material for publication: *SHELXL*97.

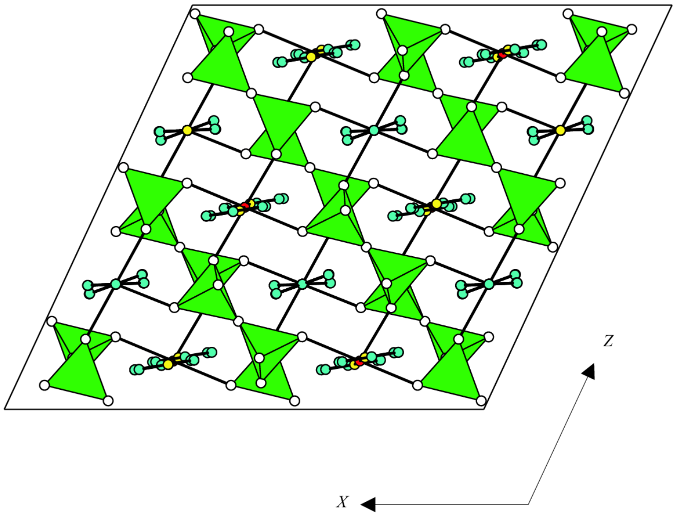

Figure 4

Projection of the structure along [010], showing atoms as spheres (Hg red, N yellow, C cyan and O white) and the dichromate group as Cr_2O_7 tetrahedra (green). For clarity, H atoms have been omitted.

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