

SHORT COMMUNICATIONS

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Redetermination of the structure of anhydrous tetrakis(ethylamine)platinum(II)dibromotetrakis(ethylamine)platinum(IV) tetrabromide, $[\text{Pt}(\text{ea})_2][\text{PtBr}_2(\text{ea})_2]\text{Br}_4$: a red analogue of Reihlen's Green. By H. ENDRES, H. J. KELLER,* B. KEPPLER, R. MARTIN, W. STEIGER and U. TRAEGER, *Anorganisch-Chemisches Institut der Universität, Im Neuenheimer Feld 270, D-6900 Heidelberg 1, Federal Republic of Germany*

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Abstract

The title compound, $\text{C}_{16}\text{H}_{56}\text{Br}_6\text{N}_8\text{Pt}_2$, crystallizes in the tetragonal space group $P4/ncc$, with $a = 11.911(4)$, $c = 12.190(3)$ Å, $Z = 2$, $V = 1730$ Å³, $d_c = 2.36$ Mg m⁻³. The structure, refined to $R = 0.052$ for 556 counter data, can best be described as a Wolfram's salt analogue and is very similar to that found in an earlier determination. Four alternating Pt–Br distances are found along the chains [Pt^{IV}–Br(1) = 2.284(7), Pt^{IV}–Br(2) = 2.684(6), Pt^{II}–Br(1) = 3.811(7) and Pt^{II}–Br(2) = 3.411(6) Å], but the platinum positions do not need to be split. The chain Br atoms are ordered one-dimensionally, all other atoms three-dimensionally.

Introduction

We are presently investigating structures of new Wolfram's salt analogues (Keller, Martin & Traeger, 1978; Endres, Keller, Martin & Traeger, 1979; Endres, Keller, Martin, Traeger & Novotny, 1980; Endres, Keller, Martin, Nam Gung & Traeger, 1979). Comparing more recent data for Pt–halogen separations with the values reported by Craven & Hall (1966) in an earlier investigation of the title compound, we realized that their values did not fit with common trends in the Pt–halogen distances in this class of compounds. In particular, the fact that two half-occupied Pt positions have been found seemed doubtful. This prompted us to prepare a crystal of this compound and to reinvestigate its structure.

Rotating-crystal photographs around the c axis (needle axis) (Cu $K\alpha$ radiation) showed diffuse layer lines superimposed on Bragg reflections for $l = 2n + 1$. Contrary to the observations of Craven & Hall (1966) we could not detect diffuse reflections on Weissenberg photographs of these layer lines, probably because monochromatized radiation was not used. The photographs showed tetragonal symmetry, as reported in the previous investigation, and gave an estimate for the lattice constants.

Exact lattice parameters (see *Abstract*) were derived from the setting angles of 25 reflections centered on a Syntex R3

diffractometer. Data collection (Syntex R3, monochromated Mo $K\alpha$ radiation, Ω background–peak–background step-scan mode, $2\theta_{\text{max}} = 60^\circ$) yielded 556 observed independent reflections with $I > 3.0\sigma(I)$. These were corrected for Lorentz and polarization factors and for absorption ($\mu = 15.86$ mm⁻¹). The systematic absences ($0kl$ with $l = 2n + 1$, $hk0$ with $h + k = 2n + 1$ and hhl with $l = 2n + 1$) correspond to the space group $P4/ncc$ (D_{4h}^8). A Patterson synthesis showed the positions of Pt, the Br outside the chains and one of the half-occupied Br positions within the chain. A Fourier synthesis showed the position of the second half-occupied Br between the Pt atoms in the chain. For the heavy-atom positions and anisotropic temperature factors, R was 0.118.

A difference Fourier map revealed the positions of the ligand atoms around Pt. They were refined with anisotropic temperature factors. Refinement converged at $R = 0.052$. Atomic coordinates are listed in Table 1.† Calculations were performed with programs of the XRAY system (Stewart, Kundell & Baldwin, 1970). Scattering factors were derived from *International Tables for X-ray Crystallography* (1974).

Discussion

The bond distances and angles of the Pt complex dication are listed in Table 2. The projection of the subcell on (001) is

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34869 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^3$)

	x	y	z
Pt	250	250	162.3 (1)
Br(1)	250	250	349.7 (5)
Br(2)	250	250	442.1 (5)
Br(3)	–80.0 (2)	80.0	250
N	195 (1)	83 (1)	167 (1)
C(1)	178 (2)	24 (2)	60 (2)
C(2)	138 (2)	–97 (2)	81 (2)

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

Pt ^{IV} —Br(1)	2.284 (7)	N—Pt—Br(1)	88.5 (5)
Pt ^{IV} —Br(2)	2.684 (6)	Pt—N—C(1)	118 (1)
Pt ^{II} —Br(1)	3.811 (7)	N—C(1)—C(2)	110 (2)
Pt ^{II} —Br(2)	3.411 (6)		
Br(1)—Br(2)	1.127 (9)		
Pt—N	2.09 (1)		
N—C(1)	1.49 (3)		
C(1)—C(2)	1.54 (3)		

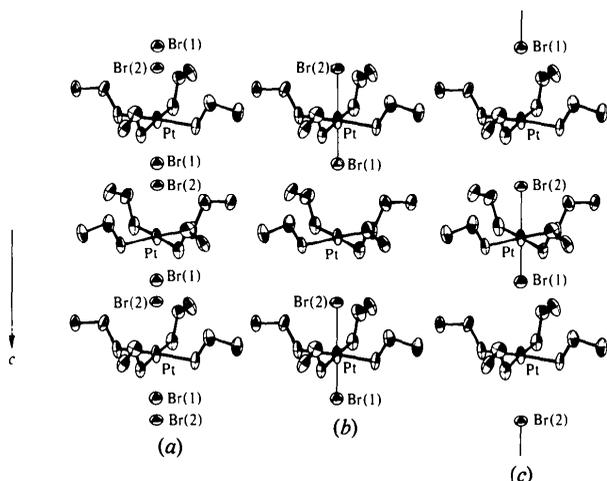


Fig. 1. (a) ORTEP plot (Johnson, 1965) of the chain, rotated 20° around the *a* axis and 40° around the *c* axis. The bromine positions drawn are statistically half-occupied. (b), (c) The same ORTEP plot showing the two possible bromine arrangements along the chain. The bromine positions drawn are fully occupied. (a) is a superposition of (b) and (c).

identical to Fig. 2 of Craven & Hall (1966). Contrary to the results of Craven & Hall (1966), we were able to refine the atomic coordinates with anisotropic temperature factors, and we found it unnecessary to split the Pt position into two half-occupied sites. When we did so, *R* increased to 0.185, and the Br atoms within the chain could not be refined with anisotropic temperature factors.

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Atomic vibrations in the magnesium difluoride crystal. By LINUS PAULING, *Linus Pauling Institute of Science and Medicine, 2700 Sand Hill Road, Menlo Park, California 94025, USA*

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Abstract

The discussion of the anisotropy parameters of the thermal vibrations of the atoms in the magnesium difluoride crystal, as determined by neutron diffraction, is facilitated by

Fig. 1(a) shows the Pt^{II}...Br—Pt^{IV} chain with the two half-occupied Br positions. This figure is quite different from that published earlier (Craven & Hall, 1966; Fig. 1), giving smaller alterations in bond distances along the chain. The differences in Pt^{IV}—Br(1) and Pt^{IV}—Br(2) distances are probably caused by repulsive interactions between Br(2) and the four methylene C atoms [C(1)] of the ligands.

To clarify the problem of one-dimensional order along the chain we have drawn the two possible arrangements of the Br atoms between the Pt atoms (Fig. 1b and c). Fig. 1(a) is the three-dimensional statistical superposition of Figs. 1(b) and 1(c). This finding is very important in interpreting the physical results — especially the resonance Raman data (Clark & Turtle, 1978) for this compound.

As pointed out by Craven & Hall the pattern of continuous diffusive layers and Bragg layers is different in nature from that in other Wolfram's salt analogues. The pattern can be interpreted as follows: The Br atoms along the chains are ordered one-dimensionally but disordered three-dimensionally. All the other atoms of the lattice (ligand atoms, Pt atoms, and Br[−] counterions outside the chains) are ordered three-dimensionally.

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recognizing that each F atom is bonded to the three nearest Mg atoms by a set of coplanar bonds with nearly the same strength, one of the bond lengths being 1.984 Å and the other two 1.994 Å.