bond will be about 10-fold faster than that of a C–T bond. Hence $k_1 \simeq 3 \times 10^3$ 1. mol^{-1} sec.$^{-1}$. For the above reaction

$$\frac{k_1}{k_{-1}} = K_{eq} = \frac{K_a[H_2O]}{K_w}$$

From this we calculate that for the reaction of the anion and water $k_1 \simeq 10^8$ 1. mole^{-1} sec.$^{-1}$.

For the analogous reaction of phenylacetylene with water, it was concluded that $k_{bi} < 2 \times 10^{-10}$ 1. mole^{-1} sec.$^{-1}$. Combining this with the pK value implies only that k for reaction of $C_6H_5C_2^-$ and H_3O^+ is less than 10^{12}. Actually by considering the expected rate for diffusion controlled neutraliza-

tion reactions,[19] we can set a limit of between 10^{10} and 10^{11} (the value for a diffusion controlled process) for this rate coefficient. Since one will surely except neutralization by H_3O^+ to be faster than by H_2O, this upper limit is probably close to the actual value.[20] It thus appears that the anion of an acetylene derivative belongs to the group of "fast" proton acceptors.[19]

(19) R. P. Bell, *Quart. Revs. (London)*, **13**, 169 (1959).

(20) For the forward and reverse of a general catalyzed proton transfer reaction, the sums of the Brönsted coefficients should equal unity. Since we have concluded that β for reaction of phenylacetylene with bases was above 0.8, it follows that α should be less than 0.2, perhaps 0.15. Some such figure as this is consistent with the above rate coefficients for reaction of the anion.

The Crystal Structure of Ethylenediamine Tribromoplatinum (C₂N₂H₈)PtBr₃[1]

BY THOMAS D. RYAN AND R. E. RUNDLE

Pt(en)Br₃ is a complex between Pt(en)Br₂ and Pt(en)Br₄. The orthorhombic crystals, $a = 5.60$, $b = 14.77$, $c = 10.12$ Å. contain Pt(IV)enBr₂ and Pt(II)enBr₂ planar (or nearly planar) groups lying parallel to (100) and connected with essentially linear, ordered, Pt(II) ⋯ Br–Pt(IV)–Br ⋯ Pt(II) ⋯ chains running along a. Between chains Pt(II) and Pt(IV) positions can be exchanged at random. The distance Pt(IV)–Br along the chains is 2.48 Å., and the average Pt(II)–Br, Pt(IV)–Br distance within the planar groups is 2.51 Å., not significantly different. Light with its electric vector along the chains is very strongly absorbed. Presumably this is a charge transfer absorption.

Introduction

The compound with the empirical formula, Pt(en)Br₃ (en = H₂NCH₂CH₂NH₂), is of interest because of its relation to the problem of the possibility of Pt(III). The structure reported here confirms the chemical evidence which has been given to show that Pt(II) and Pt(IV) in equal amounts lead to an average valence.[2] The compound is of further interest because of its strong pleochroism, the crystallographic distinction between Pt(II) and Pt(IV) and a type of disorder found in the crystal. It is far from an ideal crystal for the study of metal–ethylenediamine rings, and in our work only heavy atom positions and their relation to the points of interest above have been given attention. The heavy atoms, except for a point with respect to the disorder, are found without difficulty, and details of the structure determination are not discussed here.

Our attention was drawn to this problem by Prof. R. E. McCarley of this Laboratory, who made the compound and supplied us with crystals. The crystals form very thin, orthorhombic blades of an iridescent green. In polarized light they are light yellow when viewed with the electric vector normal to the blade axis, but black and nearly completely absorbing, even in very thin crystals, when the electric vector is along the blade axis.

The lattice constants are $a = 5.60$ (blade axis), $b = 14.77$, $c = 10.12$ Å.; $\rho_{obsd.} = 4.03$ g./cc. vs.

$\rho_{x\text{-ray}} = 4.027$ for four Pt(en)Br₃ per cell. (Lattice constants b and c were determined from back reflection Weissenberg diagrams, a from precession diagrams using b or c for internal calibration.)

Since reflections $\{hkl\}$ are observed only for $h + k = 2n$, and $\{h0l\}$ only for $h = 2n$, $l = 2n$, the possible space groups are Cmcm, Cmc2₁ and C2cm. Though platinum and bromine positions were found in Cmcm, the true space group must be C2cm if the Pt(en) rings are non-planar, as expected.[3]

Oscillation photographs taken with a as the rotation axis showed pronounced streaks between layer lines. The reason for this streaking is made clear by the structure determination (*vide infra*). Intensities $\{0kl\}$, $\{hk0\}$ and $\{h0l\}$ were determined visually from timed and/or multiple film Weissenberg and precession diagrams. Anomalous dispersion,[4] Lorentz and polarization factors were taken into account, but since no absorption corrections were made, this is a factor limiting the accuracy of the structure reported below.

Patterson functions gave platinum and rough bromine positions very simply. It was at first supposed that the twelve bromine atoms would be found in an eight-fold set and in a four-fold set, but it became evident that four of the bromine atoms must be distributed at random in an eight-fold set.

Parameters were refined using reflections from all three zones and a least squares program supplied by Templeton and Senko. The discrepancy factors, $R = \dfrac{\Sigma| \,|F_0| - |F_c|\,|}{\Sigma\,|F_0|}$ were 0.079, 0.124

(1) Contribution No. 884. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Based on a thesis submitted by T. D. R. to Iowa State University in partial fulfillment of the requirements for the degree of Master of Science.

(2) G. W. Watt and R. E. McCarley, *J. Am. Chem. Soc.*, **79**, 4585 (1957).

(3) See, for example, A. Hakahara, Y. Saito and H. Kuroya, *Bull. Chem. Soc. (Japan)*, **25**, 331 (1952).

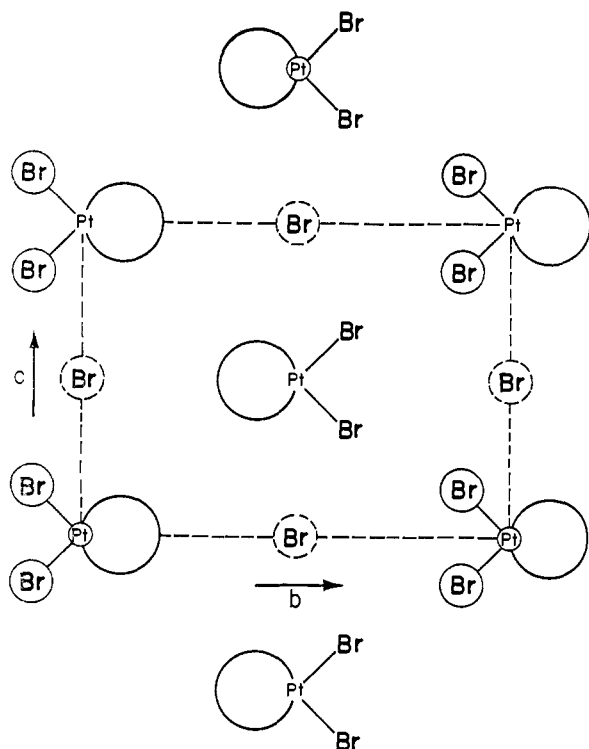(4) D. Templeton and C. H. Dauben, *Acta Cryst.*, **8**, 841 (1955).

Fig. 1.—Structure of Pt(en) Br$_2$ in the plane, $x = 0$. Dashed circles are bromine positions, randomly 0.3 Å.[3] above or below this phase. Structure on the plane $x = \frac{1}{2}$ is similar but translated by $\frac{1}{2}b$. There is no distinction between Pt(II) and Pt (IV) in these planes.

and 0.150 for $\{hk0\}$, $\{h0l\}$ and $\{0kl\}$, respectively. A total of 154 reflections were used in the refinement.[5] Final parameters are given in Table I.

TABLE I

PARAMETERS OF THE Pt(en)Br$_3$ STRUCTURE IN CMCM.

(Errors are standard deviations from least squares)

Pt in 4(c)^a $y = 0.232 \pm 0.002$
Br$_1$ in 8(f)^b $y = 0.112 \pm 0.002$ $z = 0.075 \pm 0.002$
Br$_{11}$ (bridge)^d in 8g^c $x = 0.442 \pm 0.002$ $y = 0.239 \pm 0.00$

^{a} 4(c) = $\pm(0y\frac{1}{4})$ and C-centered. ^{b} 8(f) = $\pm(0yx, 0y\frac{1}{2}-z)$ and C-centered. ^{c} 8(g) = $\pm(\bar{x}y\frac{1}{4}, \bar{x}y\frac{1}{4})$ and C-centered. ^{d} Half bromine atoms at each position in 8(g).

The structure is illustrated in Figs. 1 and 2. In Fig. 2 an ordered chain is shown running along a, with alternating Pt(II) and Pt(IV), though discrete reflections reveal no distinction between Pt(II) and Pt(IV), and the four bridging bromine atoms are split into an eight-fold set with each half-atom nearer to one of its platinum neighbors, Pt(IV), as shown by the crosses in Fig. 2. Nevertheless, in each chain along a there must be ordering, and if the composition corresponds exactly to a 1:1 complex then the ordering in one chain, for spacial reasons, must be complete. It is this necessity for one dimensional ordering that leads
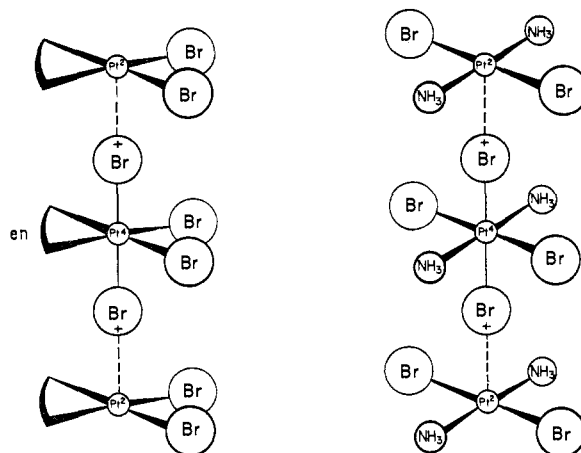
Fig. 2.—Chains in Pt(en)Br$_3$ and Pt(NH$_3$)$_2$Br$_3$. Crosses give alternate positions for bridging bromines, but there is ordering along each chain.

to the rather strong streaks between layer lines on a-axis rotation diagrams. In going from one chain to another, however, the Pt(II) and Pt(IV) are arranged at random, otherwise the streaks would resolve into discrete spots, and a would have to be doubled.

The correspondence with the structure and the disorder of Pt(NH$_3$)$_2$Br$_3$ is pronounced, as illustrated in Fig. 2.[6] In this case also an apparent Pt(III) arises from a stochiometric complex of Pt(II) and Pt(IV) molecules.

One might expect to find a difference between Pt(II)–Br and Pt(IV)–Br distances within the Pt(en)Br$_2$ planes, but evidence for this is lacking. Fourier peaks for Br$_1$ were symmetrical and difference peaks gave no indication of resolution. The temperature factor for Br$_1$ is about twice that for the bridge bromine atoms, but the latter are more thoroughly tied down, and the lack of absorption corrections makes conclusions unreliable. A very similar situation was found by Hall and Williams in Pt(NH$_3$)$_2$Br$_3$, and indeed their Pt–Br distances are in good agreement with ours. (See Table II.)

TABLE II

(Errors are standard deviations from least squares)

	Pt(NH$_3$)$_2$Br$_4$	Pt(en)Br$_3$
PtIV–Br (chain)	2.50 Å.	2.48 $\pm$ 0.01 Å.
PtII....Br (chain)	3.05	3.125
PtIV–Br (molecular plane)	$\{2.45$	$2.51 \pm 0.04\}^a$
PrII–Br		
Br–Br (in plane)		3.45
Br–Pt–Br		89° 54'

^{a} Not distinguishable.

In spite of the inadequate absorption corrections we believe these two structures provide strong evidence that the difference between Pt(IV)–Br and Pt(II)–Br distances is quite small, in contrast to Brosset's findings.[4] That there should be disordering of Pt(IV) and Pt(II) positions for both cis and trans PtBr$_2$ groups is added evidence that distance differences are very small. The limited

(6) D. Hall and P. P. Williams, Acta Cryst., 11, 624 (1958). C. Brosset, Archiv. Kemi, Min. Geol., 26A, No. 19 (1948).

data available also support small difference in Pt-(II)–Cl and Pt(IV)–Cl distances.[7]

The strong absorption of light in this compound occurs with the electric vector along the Br–Pt-(IV)–Br···Pt(II)···Br–Pt(IV)–Br···chains. This absorption is, then, related to the many other known compounds where a halogen bridge links two different oxidation states of the same element.[8]

(7) L. Sutton, et al., "Interatomic Distances," The Chemical Society, London, 1958, pp. 100–101.

(8) See, for example, N. Elliot and L. Pauling, J. Am. Chem. Soc.,

Presumably this is a charge transfer spectrum of the type first described by Mulliken,[9] and the strong polarization is evidence that the transfer is through the bridging halogen from Pt(II) to Pt(IV) and is accompanied by a greater contribution of bridge halogen bonding to Pt(II) in the excited state.

60, 1846 (1938); A. J. Cohen and N. Davidson, ibid., 73, 1955 (1951), and S. Yamada and R. Tsuchida, Bull. Chem. Soc. (Japan), 29, 894 (1956).

(9) R. S. Mulliken, J. Am. Chem. Soc., 72, 600 (1950) and 74, 801, 811 (1952).

Magnetic Compounds of Hexavalent Rhenium with the Perovskite-type Structure

BY JOHN LONGO AND ROLAND WARD

Phases of composition $A^{II}(B_{.5}{}^{II}Re_{.5}{}^{VI})O_3$ have been prepared by interaction of metal oxides under controlled conditions. When A^{II} is barium and B^{II} represents the divalent cations Ca, Mg, Mn, Fe, Co, Zn and Cd, the compounds are all of the cubic ordered perovskite type. The compounds with manganese and iron are magnetic. Substitution of strontium and calcium in the A position when B^{II} is iron leads to distorted structures apparently related to the cubic perovskite type. The approximate Curie temperatures for the magnetic phases have been determined.

The relationship of the structure of compounds such as $Ba_3TaO_{5.5}$,[1] Ba_2ZnWO_6[2] and Ba_2NaReO_6[3] to the perovskite structure has been described in previous publications. The structure is indicated by the formula $A^{II}(B^n_{.5}B_{.5}{}^{VIII-n})O_3$. The B cations are arranged in a simple cubic lattice joined through oxygens. The A cations are at the centers of the cubes. When $n = 1$ or 2, the different B cations assume alternate positions in the cubic lattice as indicated in Fig. 1. The length of the unit cell edge is twice that of the simple perovskite. The ordering of the B cations apparently depends on the charge difference between the two different B ions for in the compound $Ba(Fe_{.5}Ta_{.5})O_3$ (where $n = 3$) there is no evidence for the larger unit cell. The size factor also plays a part, however, for the compound $Ba(La_{.5}Ta_{.5})O_3$[4] has the ordered perovskite structure. The system is rendered somewhat more flexible by the possibility of oxygen deficiencies.[1]

It is interesting to note that of all of the compounds with this structure hitherto reported none contained more than one paramagnetic cation. In view of the current interest in magnetic interaction of cations in mixed oxides, it seemed to us that the ordered perovskite structure should provide some interesting phases if both B cations could be paramagnetic. The importance of having a large charge difference pointed to the use of such ions as Mo^{+5}, Re^{+6}, Os^{+6} in combination with suitable paramagnetic divalent cations of the first transition period. Some indications have been found that osmium and molybdenum are capable of forming such phases but the greatest success has been with hexavalent rhenium. This paper describes the preparation and characterization of some of these compounds.

(1) F. Galasso, L. Katz and R. Ward, J. Am. Chem. Soc., 81, 820 (1959).

(2) E. J. Fresia, L. Katz and R. Ward, ibid., 81, 4783 (1959).

(3) A. W. Sleight and R. Ward, ibid., 83, 1088 (1961).

(4) L. H. Brixner, ibid., 80, 3214 (1958).

TABLE I

X-RAY POWDER DIFFRACTION DATA FOR $Ba(Co_{.5}Re_{.5})O_3$ INDEXED ON THE BASIS OF THE ORDERED PEROVSKITE STRUCTURE ($a = 8.086$ Å.) AND A COMPARISON OF OBSERVED AND CALCULATED INTENSITIES

hkl	$Sin^2\theta$, obsd.	$Sin^2\theta$, calcd.	I, obsd.	I, calcd.
111	0.0270	0.0272	11.9	13.1
220	.0723	.0726	96.3	100.0
311	.0997	.0999	8.8	8.9
222	.1088	.1090	3.2	2.3
400	.1452	.1453	32.0	30.5
331	.1725	.1725	3.8	4.1
422	.2178	.2179	39.7	41.8
333	.2455	.2452	3.6	3.2
511				
440	.2906	.2906	19.4	18.2
531	.3179	.3178	3.7	3.1
620	.3632	.3632	17.6	18.2
444	.4356	.4358	5.2	6.2
711	.4634	.4631	2.1	1.8
551				
642	.5096	.5085	21.2	23.3
731	.5361	.5357	2.4	2.3
553				
800	.5812	.5811	3.8	3.4
822	.6536	.6538	13.2	15.1
660				
840	.7262	.7264	11.6	13.8
664	.7988	.7990	10.0	11.7
844	.8716	.8717	15.4	19.2
10,20	.9439	.9443	50.0	66.9
862				

Experimental

The barium oxide used was prepared by heating the peroxide (92.78%) at 950° in vacuum for 24 hrs. while the strontium oxide was prepared by heating the carbonate in a stream of hydrogen at 1150° for 48 hr. Nickelous oxide was prepared by heating the carbonate in air at 1250°, cobaltous oxide by heating the carbonate in a carbon dioxide atmosphere, manganous oxide by heating manganese dioxide in a stream of hydrogen at 900° for 36 hr. The calcium oxide, magnesium oxide, cadmium oxide, zinc oxide,