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Preparation and Structural Investigation of Some New Wolffram's Salt Analogues: $[Pt(L{-}L)_2][Pt(L{-}L)_2X_2](ClO_4)_4$

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The preparation of some new Wolffram's Red Salt analogues of stoichiometry $[Pt(L{-}L)_2[Pt(L{-}L)_2X_2](ClO_4)_4$ *with L–L = 1,2-diaminoethane (en) or 1,2-diaminopropane (dapn) and X = Cl, Br or I is described. The unit cell data of these compounds as derived from powder diagrams indexed by the aid of rotating crystal and Weissenberg photographs are reported. These are compared with earlier findings on other types of these salts. The metal–metal separations along the linear M–X–M chains increase slightly in going from the chlorine to the bromine and iodine derivatives. But the differences in the alternating* $M^{IV}{-}X{-}{-}M^{II}$ *distances along the chain are reduced with increasing size of the halogen. The two compounds* $[Pt(en)_2][Pten_2X_2](ClO_4)_4$ *with X = Cl and Br are ordered three dimensionally.*

Introduction

There arose much recent interest in the chemistry and physics of linear chain transition metal compounds because of their very anisotropic physical properties [1–3]. Wolffram's Red Salt and its analogues are linear chain transition metal compounds which contain halide bridged linear arrays of alternating platinum(II) and platinum(IV) complex units [4–9]. As shown in a schematic drawing of their general structure (Figure 1) no direct metal–metal contacts occur in the lattice, and these compounds can be grouped in class II of Robin and Days general scheme of mixed valence solids [10]. By introducing the less coordinating counterion perchlorate via addition of $AgClO_4$ or $HClO_4$ to the Wolffram's Salt solution it was tried to remove the halide ions and to obtain compounds with direct metal–metal contacts. As shown in the following the halide ions are exchanged only partly leaving one bridging halide per platinum in the lattice. The unit cell data of the products of stoichiometry $[Pt(L{-}L)_2][Pt(L{-}L)_2X_2](ClO_4)_4$ (with L–L = 1,2-diaminoethane (en) and 1,2-diaminopropane (dapn) and X = Cl^-, Br^-, I^- and their special features are discussed and compared with the other known compounds of this type.

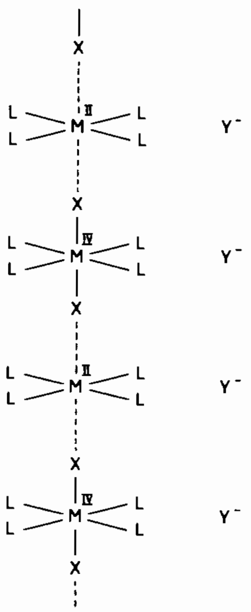

Figure 1. The general structure of Wolffram's Salt type compounds.

Experimental

Preparation of Compounds

$Pten_2Cl_4$ [11], $Pten_2Br_2$ [12], and $[Pt(en)_2][Pt(en)_2Cl_2](ClO_4)_4$ [13] were obtained by the procedures described earlier. The latter compound was obtained as purple or red crystals, (as described by Kida [13]) depending on the chloride concentration of the solution. But recrystallization from diluted perchloric acid yielded dark green needles. All these forms were shown to be identical by their X-ray single crystal and powder patterns. Least squares fits of the powder counter diagrams of the purple and the green forms showed no differences in the lattice constants within standard deviations. Determination of the water content yielded less than 0.2 per cent H_2O per Pt atom for the purple and the green crystals, so we think that there is no detectable amount of crystal water in the lattice. $Pt(en)_2Br_4$ was prepared by addition of bromine water to an aqueous solution of $Pt(en)_2Br_2$. All these compounds were identified by their C, H, N analyses.

$Pt(en)_2Cl_2$

This was obtained by stirring an aqueous solution of 3 g K_2PtCl_4 and 4.5 g 1,2-diaminoethane for one hour at room temperature. The precipitated $PtenCl_2$ was filtered and washed with cold water. A slurry of this product in water was prepared to which an excess of the 1,2-diaminoethane base was added. This mixture was stirred at 40 °C until a clear solution was obtained which was evaporated under vacuum to dryness. The residue was dissolved in water and neutralized with diluted hydrochloric acid. On addition of five volumes of ethanol to this solution the colorless $Pt(en)_2Cl_2$ precipitated. It was washed with ethanol and ether. The product was recrystallized from water to obtain colorless needles.

$[Pt(en)_2]\,[Pt(en)_2Br_2](ClO_4)_4$

a) Equimolar amounts of $Pt(en)_2Br_2$ (50 mg) and $Pt(en)_2Br_4$ (67 mg) were dissolved in 30 ml of hot water. 0.5 ml of 1 molar aqueous perchloric acid solution was added. On concentrating green dichroic needles precipitated. They were filtrated, washed with alcohol and recrystallized from water. *Anal.* % C found 8.15 (calc. 8.10), % H 2.79 (2.69), % N 8.75 (9.43).

b) The preparation of the compound $[Pt(en)_2]$ $[Pt(en)_2Br_2](ClO_4)_4$ could be achieved by starting from $Pt(en)_2Cl_2$ as well. $Pt(en)_2Cl_2$ was dissolved in water and the solution divided into two equal parts. To one of them bromine water was added and the excess bromine removed by evacuation and boiling. Then this solution was mixed with the $Pt(en)_2Cl_2$ solution together with a corresponding amount (see above procedure) of 1 molar aqueous perchloric acid. On concentration by evaporation *in vacuo* the green dichroic needles of stoichiometry $[Pt(en)_2]$ $[Pt(en)_2Br_2](ClO_4)_4$ were obtained.

$[Pt(en)_2]\,[Pten_2I_2](ClO_4)_4$

To an aqueous solution of 50 mg $Pt(en)_2Cl_2$ an excess of iodine dissolved in ethanol was added. The solution was concentrated on a vacuum evaporator to remove excess iodine and then treated with a solution of 50 mg $Pt(en)_2Cl_2$, 66 mg $NaClO_4$ and 0.5 ml 1 molar aqueous $HClO_4$. On concentrating golden lustrous and dichroic needles were obtained. Recrystallization from diluted perchloric acid yields golden needles or highly dichroic golden plates of formula $[Pt(en)_2]\,[Pten_2I_2](ClO_4)_4$. *Anal.* % C found 7.51 (calc. 7.49), % H 2.58 (2.50), % N 8.51 (8.73).

The compounds $[Pt(dapn)_2]\,[Pt(dapn)_2X_2]$ $(ClO_4)_4$ (X = Br, I) were prepared in an analogous way using 1,2-diaminopropane as ligand.

X-Ray Investigations

The elongated crystals were mounted along their long axis, which in all cases proved to be parallel to the metal–halogen–metal chains. Unit cell data were first derived from rotating crystal and Weissenberg photographs taken with CuK_α and CoK_α radiation. Powder counter diagrams taken with CuK_α radiation were indexed using the lattice constants obtained by the single crystal photographs. Then the lattice constants were recalculated from the powder diagrams using a least squares routine [14].

Results and Discussion

Compounds $[Pten_2]\,[Pten_2X_2](ClO_4)_4$

Crystal data are listed in Table I. The crystals of the chloro compound are orthorhombic, systematically extinct reflections (hkl with h + k + l = 2n + 1, hk0 and 0kl with k = 2n + 1) are consistent with space groups Iba2 and Ibam. The crystals of the bromo and the iodo compounds are monoclinic,

TABLE I. Crystal Data of Compounds $[Pten_2]\,[Pten_2X_2](ClO_4)_4$. Axes in Å.

X System	Cl Orthorhombic		Br Monoclinic	I Monoclinic	
a	9.81(2)^a	9.84(2)^b	8.061(8)	7.85(3)^c	7.8 (1)^d
b	10.90(1)	10.82(4)	11.149(7)	6.05(4)	5.92(8)
c	13.65(1)	13.60(2)	8.61 (1)	9.53(5)	9.6 (2)
β			108.77 (8)°	93.0 (4)°	94 (1)°
Number of Lines	24	19	37	18	13

^{a}Green form. ^{b}Purple form. ^{c}Platelets. ^{d}Needles.

TABLE III. Crystallographic Findings of Wolffram's Red Analogue Compounds.

	Repeating Distance in Chain Direction (Å)	1-D Superstructure	M–M Separation (Å)	Bond Lengths (Å) M–X	——M	Reference
Chloro Compounds						
$[Pt(NH_2C_2H_5)_4][Pt(NH_2C_2H_5)_4Cl_2]Cl_4$ "Wolffram's Red"	5.39	yes	5.39	2.26	3.13	17
$[PtenCl_2][PtenCl_4]$	5.481	no	5.481	–	–	6
$[Pd(NH_3)_2Cl_2][Pd(NH_3)_2Cl_4]$	5.21	yes	–	1.99	3.22	15
$[(Pd, Pt)(NH_3)_2Cl_2][Pd, Pt)(NH_3)_2Cl_4]$	5.33	yes	–	2.03	3.30	15
$[Pten_2][Pten_2Cl_2](ClO_4)_4$	10.90[a]	no	5.45	–	–	this work
Bromo Compounds						
$[Pt(NH_3)_2Br_2][Pt(NH_3)_2Br_4]$	5.53	yes	5.53	2.50	3.03	16
$[Pt(NH_2C_2H_5)_4][Pt(NH_2C_2H_5)_4Br_2]Br_4$	12.14	yes	6.07	2.42	3.19	4
				2.46	4.07	
$[Pt(NH_2C_2H_5)_4][Pt(NH_2C_2H_5)_4Br_2]Br_4 \cdot 4H_2O$	5.586	yes	5.686	2.479	3.139	7
				2.447	3.107	
$[Pt(NH_2C_2H_5)_4][Pt(NH_2C_2H_5)_4Br_2]Br_4 \cdot 4H_2O$	5.606	yes	5.606	–	–	8
$[PtenBr_2][PtenBr_4]$	5.60	yes	5.60	2.48	3.125	18
$[PtenBr_2][PtenBr_4]$	5.606	no	5.606	–	–	6
$[Pt(NH_3)_2Br_2][Pt(NH_3)_2Br_4]$	5.54	yes	–	2.17	3.37	15
$[Pten_2][Pten_2Br_2](ClO_4)_4$	11.15	no	5.57	–	–	this work
$[Ptdapn_2][Ptdapn_2Br_2](ClO_4)_4$	5.64	yes	5.64	–	–	this work
Iodo Compounds						
$[PtenI_2][PtenI_4]$	5.862	no	5.862	–	–	6
$[Pten_2][Pten_2I_2](ClO_4)_4$	6.05[b]	yes	6.05	–	–	this work
$[Ptdapn_2][Ptdapn_2I_2](ClO_4)_4$	5.8	yes	5.8	–	–	this work
$K_4[PtI_4][PtI_6]$	5.92	no	5.92	2.74	3.18	19
$[Pt(NH_2C_2H_5)_4][Pt(NH_2C_2H_5)_4I_2]I_4$	12.732	?	6.366	–	–	8

[a] Green form. [b] Platelets.

showing no detectable systematic extinctions. The iodo compound can be obtained as platelets and as needles. Both forms seem to be identical within the standard deviations of their lattice constants. On rotating crystal photographs of the iodo compound diffuse layer lines can be detected between the normal layer lines, indicating a one-dimensional superstructure of 2b along the b-axis. On photographs of the chloro and the bromo compounds instead of the diffuse layer lines normal though very weak Bragg layer lines can be discerned. From this feature we may conclude that the metal–halogen–metal chains are ordered in three dimensions.

TABLE II. Crystal Data of Compounds $[Pt(dapn)_2]$ $[Pt(dapn_2)_2X_2](ClO_4)_4$.

X System	Br Orthorhombic	I Orthorhombic
a	8.00 (1) Å	7.66(1)
b	5.640(6) Å	5.80(2)
c	19.87 (2) Å	20.02(4)
Number of Lines	18	17

Compounds $[Pt(dapn)_2]$ $[Pt(dapn)_2X_2](ClO_4)$

Crystal data are summarized in Table II. Both compounds show the systematic absence of reflections hkO with h = 2n + 1 and Okl with l = 2n + 1. Rotating crystal photographs exhibit the diffuse layer lines caused by the one-dimensional superstructure along the metal–halogen–metal chains.

From the summary of crystallographic findings given in Table III it becomes clear that the distance between two halogen bridged metal atoms is rather independent from the equatorial amine ligands and depends mainly on the size of the halogen atom and possibly on the counter ions and water content in the lattice. The increase of the metal–metal separations is due to a corresponding elongation of the direct M–X bonds, whereas the lengths of the charge-transfer M——X bonds are rather unaffected. This means that the electronic interaction along the metal–halogen charge-transfer bond augments with the size of the halogen. This was also pointed out recently by Textor and Stieger [8].

The data of Table III are also interesting from a structural point of view. In none of the structural investigations reported in the literature could a three dimensional order with a repeat distance of two metal–metal separations along the chain be found. Instead diffuse layer lines between the normal Bragg layer lines indicate one-dimensional order along the M–X——M chain only. In contrast to those findings we could detect very weak Bragg layer lines with the compounds $[Pten_2][Pten_2X_2](ClO_4)_4$, X = Cl, Br. The variation of the intensity of the different layer lines is: k = 2n + 1 very weak, k = 4n + 2 medium, k = 4n strong. This indicates a three dimensionally ordered structure with a repeat distance of two metal–metal separations along the chain.

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