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Crystal Structures of Bromo-Bridged One-Dimensional Mixed-Metal Compounds, $[Ni^{II}(en)_2][Pt^{IV}Br_2(en)_2](ClO_4)_4$ and $[Pd^{II}(en)_2][Pt^{IV}Br_2(en)_2](ClO_4)_4$

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The metal-alternated linear chain structures of the title compounds have been determined by X-ray analyses. Their structural parameters along the chains in the hetero-metal systems show weak $M^{II}\cdots M'^{IV}$ interactions compared with the homo-metal systems.

Halogen-bridged one-dimensional M^{II}-M^{IV} mixed-valence compounds have attracted much interest from the viewpoints of solid state physics and chemistry of low-dimensional compounds.[1] Their solid state properties have been extensively studied as functions of bridging halogen and metal atoms.[2] Recently, analogous compounds containing hetero-metal atoms were synthesized and their properties were studied by some workers.[3-5] In this study, we have determined the structural parameters along the chain by X-ray crystal structure analysis.

Crystals of $[Ni(en)_2][PtBr_2(en)_2](ClO_4)_4$ 1 and $[Pd(en)_2][PtBr_2(en)_2](ClO_4)_4$ 2 suitable for X-ray work were obtained by mixing the appropriate aqueous solutions of $[M^{II}(en)_2]^{2+}$ (M=Ni for 1 and Pd for 2), $[Pt^{IV}Br_2(en)_2]^{2+}$, and $NaClO_4$.[3] The crystal data are: for 1, monoclinic, C2/c, a=16.639(2), b=10.930(3), c=16.628(3) Å, β=109.65(1)°, V=2847.9(10) Å^3, Z=4, R=0.044 for 2091 reflections;[6] for 2, orthorhombic, Icma, a=13.556(3), b=11.003(3), c=9.664(2) Å, V=1441.5(6) Å^3, Z=2, R=0.027 for 850 reflections.

Figure 1 shows the crystal structure of the monoclinic cell of 1, together with its orthorhombic subcell.[6] The crystal of 2 is isomorphous with $[Pd(en)_2][PdX_2(en)_2](ClO_4)_4$ (X=Cl[7] and Br[8]) and its structure is the same as the orthorhombic subcell, in which the sites of M^{II} and M^{IV} complexes are disordered and can not be identified. In contrast to the disordered structure of 2, Ni and Pt atomic sites in 1 are crystallographically identified, which are alternately stacked along the chain parallel to the b axis. The X-ray analysis of 1 revealed the partial disorder between the Ni and Pt atoms on the metal sites[9] and of the bridging Br atoms. Occupancy factors of the disordered atoms are, however, explained by the structure comprised of the octahedral six-coordinated $[Pt^{IV}Br_2(en)_2]^{2+}$, square-planar four-coordinate $[Ni^{II}(en)_2]^{2+}$ units and ClO_4^- ions. Judging from the above crystallographic consideration, it is concluded that the Pt^{IV} and Ni^{II} complexes are alternately stacked in the crystal of 1, constructing the metal-alternated linear chains of $\cdots Ni^{II}\cdots Br\text{-}Pt^{IV}\text{-}Br\cdots$ segments. By analogy with 1, a chain

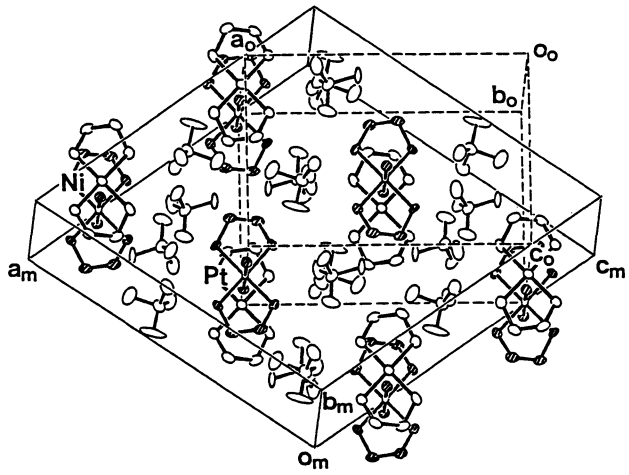

Fig. 1. Perspective view of the monoclinic cell of $[Ni(en)_2][PtBr_2(en)_2](ClO_4)_4$, together with the orthorhombic subcell indicated by broken lines. Disordered atoms with minor occupancies are omitted for clarity.

Table 1. Average bond distances (Å)

	1	2
Pt^{IV}-Br	2.465(1)	2.467(1)
$M^{II}\cdots$Br	3.000(1)	3.035(1)
Pt^{IV}-N	2.021(7)	2.051(4)
M^{II}-N	1.939(17)	

structure of $\cdots Pd^{II}\cdots Br\text{-}Pt^{IV}\text{-}Br\cdots$ is expected for 2. These structures are well consistent with the results of XPS[3] and EXAFS[4] studies.

Selected interatomic distances are listed in Table 1. Pt^{IV}-Br distances (2.465(1) Å in 1 and 2.467(1) Å in 2) are slightly shorter than that in $[Pt(en)_2][PtBr_2(en)_2](ClO_4)_4$ (2.473(1) Å).[10] $Pd^{II}\cdots$Br distance of 3.035(1) Å in 2 is, on the contrary, significantly longer than that of 2.911(1) Å in $[Pd(en)_2][PdBr_2(en)_2](ClO_4)_4$.[8] This indicates that the $Pd^{II}\cdots$Br interaction, namely the $Pd^{II}\cdots Pt^{IV}$ interaction in the hetero-metal system, is weaker than the corresponding interactions in the homo-metal systems, which is well in agreement with the solid state properties observed for the mixed-metal compounds.[11]

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6) When the weak reflections having diffuse spots are omitted, the crystal of 1 can be considered to be orthorhombic, Icma, a=13.599(2), b=10.927(3), c=9.582(1) Å, V=1423.9(4) Å^3, Z=2, R=0.030 for 788 reflections, and occupancy factors of Pt and Ni atoms are 0.516(4) and 0.484, respectively.
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