07-Crystallography of Organometallic and Coordination Compounds

PS-07.01.15 CRYSTAL STRUCTURES OF THREE DIASTEREOMERIC COMPLEXES FROM [1-[1-(DIMETHYLAMINO)ETHYL]-2-NAPHTHALENYL-C,N]PALLADIUM(II) AND N,N,N',N'-TETRAMETHYL-2,3-BUTANEDIAMINE.

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It has been shown that the optically active bis-(acetonitrile)[1-[1-(dimethylamino)ethyl]-2-naphthalenyl-C,N]palladium(II) perchlorate is a versatile reagent as an indicator of the enantiomeric excess of optically active diamines. The S-isomer of this palladium compound has been reacted with the R,S-, R,R- and S,S- enantiomers of N,N,N',N'-tetramethyl-2,3-butanediamine to produce the three diastereomers the structures of which have been determined using single crystal X-ray diffraction.

Crystal data : $[(CH_3)_2NCH(CH_3)C_{10}H_6Pd(CH_3)_2NCH(CH_3)$-
$CH(CH_3)N(CH_3)_2]ClO_4$

1. (S,R,S)-isomer, monoclinic, space group $P2_1$, a = 11.661(3), b = 9.982(2), c = 13.227(4)Å, β = 105.29(2)°, Z = 2, R = 0.032.
2. (S,R,R)-isomer, orthorhombic, space group $P2_12_12_1$, a = 7.872(3), b = 15.843(5), c = 20.273(2)Å, Z = 4, R = 0.037.
3. (S,S,S)-isomer, monoclinic, space group $P2_1$, a = 7.978(2), b = 20.856(2), c = 15.218(2)Å, β = 92.06(2) , Z = 4, R = 0.036.

The unit cell of the (S,S,S)-isomer contains 2 pairs of molecules which differ slightly in bond distances and bond angles. The configuration around the palladium atom is distorted square planar in all the three diastereomers.

Simon Y M Chooi, Pak-Hing Leung, Chin Chin Lim, K F Mok, G H Quek, K Y Sim and M K Tan, Tetrahedron: Asymmetry, 3, 529-532, 1992.

PS-07.01.16 REACTION RATE DEDUCED FROM STRUCTURAL CHANGE IN CRYSTALLINE-STATE PHOTOISOMERIZATION

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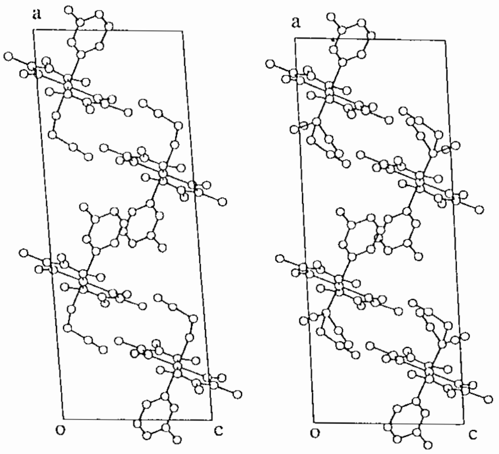
It has been found that the β-cyanoethyl (β-ce) group in cobaloxime complexes is transformed to α-cyanoethyl (α-ce) group when the complex is exposed to visible light in the solid state. Among the complexes with various base ligands, (β-ce)(3-methylpyridine)cobaloxime forms mixed crystals with the photoproduct α-ce complex in any composition. A crystal of the β-ce complex was mounted on a Rigaku AFC-5R diffractometer and was irradiated with a Xe lamp. The lattice constants, measured by the diffractometer at a constant interval, showed a gradual change. After about 75h exposure, the change became significantly small. The three-dimensional intensity data were collected. The analyzed structure revealed the disordered form of the β- and α-ce groups. Figure 1 shows the crystal structures before and after the irradiation. This clearly indicates that the β-ce group is isomerized to the α-ce group keeping a single crystal form. The reaction rate was estimated from the change of the cell parameters at early stages since the change is well-explained by first-order kinetics. The rate constant is 1.4×10^{-5} s^{-1}.

A similar experiment was perfomed for the mixed crystal which containes β-ce and α-ce complexes with a ratio of 6 : 4. The cell dimensions are approximately the same as those of the photo produced crystal with the same ratio. The change of the cell dimensions at early stages are also explained by first-order kinetics and the rate constant was calculated to be 1.8×10^{-5} s^{-1}.

Such a crystalline-state photoisomerization has been examined for the crystals of the β-ce complexes with 3-chloropyridine and 3-bromopyridine as axial base ligands. The results are compared among the three crystals.



(a) (b)

Fig. 1 Crystal structures (a) before and (b) after the irradiation

PS-07.01.17 CRYSTALLOGRAPHIC INVESTIGATION OF 15-CROWN-5 COMPLEXES OF CdX_2 (X = Cl, Br, I, NO_3).

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This presentation will focus on factors influencing in-cavity versus out-of-cavity coordination of 15-crown-5 to Cd^{2+}. The effects of anion type, solvent, and competing cations on metal ion coordination and crown ether conformation will be highlighted.

Cd^{2+} generally adopts a pentagonal bipyramidal geometry when it resides in the 15-crown-5 cavity. This has been observed in $[(CdCl_2)_2CdCl_2(\text{15-crown-5})]_n$, $[Cd(\text{15-crown-5})(OHMe)(\mu\text{-}Br)CdBr_3]$, and $[Cd(OH_2)_2(\text{15-crown-5})][CdI_3(OH_2)_2]\cdot2(\text{15-crown-5})\cdot2CH_3CN$. The characteristics of the anion, however, can greatly influence the final metal ion environment. The Cd^{2+} centers in $[Cd(\text{15-crown-5})(\mu\text{-}Br)_2CdBr(\mu\text{-}Br)]_2$ and $[Cd(NO_3)_2(\text{15-crown-5})]$ are displaced from the cavity of the ether due to the