07-Crystallography of Organometallic and Coordination Compounds

PS–07.01.11 X-RAY STRUCTURE DETERMINATION OF THE NATIVE CRYSTAL OF BLUE FLOWER PIGMENT, COMMELININ, FROM *COMMELINA COMMUNIS*

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Commelinin is a blue color pigment from blue-flower, *Commelina communis* (Japanese name : *Tsuyukusa*). It is a metalloanthocyanin that consists of six malonylawobanins, six flavocommelinins and two magnesium ions, with a molecular weight of about 9000 dalton. We have already reported the structure determination of Cd-commelinin, in which the complexation metal, Mg^{2+}, is replaced with Cd^{2+} (Kondo *et al.*, Nature, 1992, 358, 515-518). In that study, we reported that Commelinin is a novel type of supramolecule; a stoichiometric association of small molecules and metal ions. Recently, we have succeeded to solve the three-dimensional structure of the native form of commelinin; Mg-commelinin.

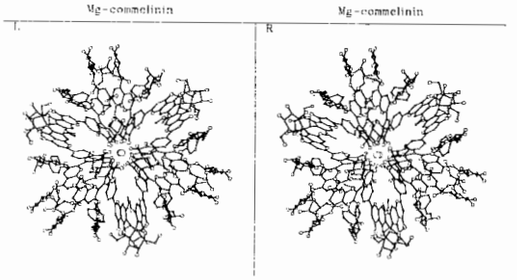
Crystals are obtained from an aqueous-ethanol solution. Its space group is *P*321 with cell dimensions a=b=31.191Å and c=33.623Å. Mg-commelin crystals are isomorphous with Cd-commelin crystals.

Diffraction data of Cd-commelinin was collected using the Weissenberg camera for macromolecular crystallography (Sakabe, *Nucl. Inst. Methods*, 1991, **A303**, 448-463) with imaging plates (Miyahara *et al.*, 1986, *Nucl. Inst. Methods*, **A246**, 572-578) at the BL-6A$_2$ station in the Photon Factory, KEK. Diffraction data was collected using a wavelength of 1.04Å to a resolution of 0.75Å. Total of 24068 independent reflections with a merging R-factor (based on F^2) of 5.62 %.

The Cd-commelinin structure had been obtained using the SHELXS-86 (Sheldrick, *Acta Cryst.*, 1990, **A46**, 467-473) program and the difference Fourier technique. This structure was used for the starting model of the refinement of Mg-commelinin giving a crystallographic R-value of 35.6% at 1.0Å resolution. After several cycles of crystallographic least-squares refinement using the XTAL program system (Hall and Stewart, 1990, *Xtal3.0 Reference Manual*) and model reconstruction on the graphics, the refined structure of Mg-commelin was obtained. The present R-factor is 12.5% at 1.0Å resolution (10533 reflections). The model includes 33 water molecules without hydrogen atoms for structure factor calculation. Anisotropic thermal parameters are applied to 209 atoms where the isotropic thermal factors, U, were smaller than 0.2.

Overall structure of Mg-commelinin is similar to that of Cd-commelinin. Two magnesium ions are located (4.9Å apart) in the center of the molecules. Three malonylawobanin molecules are coordinated to each magnesium ion, and its coordination style is a twisted prism type. The metal-to-metal distance of magnesium is significantly shorter than that of cadmium (5.1Å apart). And metal-to-coordinating oxygen distance of Mg-commelinin (1.21Å) is also significantly shorter than that of Cd-commelin (1.28Å). Small rearrangement of malonylawobanins and flavocommelinins around the metal ions are observed.

Blue coloration of commelin is basically caused by the coordination of anthocyanins to metal ions and the formation of the supramolecule. The supramolecule is stablized due to coordination, hydrophobic and hydrophilic interactions.



PS–07.01.12 CRYSTAL STRUCTURES OF OXO AND IMIDO COMPLEXES OF RUTHENIUM AND OSMIUM PORPHINS.

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We have synthesised, studied the reactivity and carried out molecular orbital calculations and structural analysis the following three metal porphin complexes:

1. [Ru($N_4C_{20}H_8$(PhMe)$_4$(NH$_2$terBu)$_2$]
2. [Os($N_4C_{20}H_8$(PhCl)$_4$(NH$_2$terBu)$_2$] and
3. [Os($N_4C_{20}H_8$(PhMe)$_4$(NterBu)O]EtOH.

Their crystal structures will be presented and the molecular dimensions and geometry will be compared and discussed.

The crystal data and the ORTEP drawing of the oxo complex of osmium porphin are given as follows:

Compound	1.	2.	3.
Formula	$C_{nn}H_{58}N_nRu$	$C_{52}Cl_4H_{46}N_6Os$	$C_{54}H_{51}N_5O_2Os$
M	916.20	1087.00	992.24
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
a , Å	13.808(3)	11.046(2)	13.546(6)
b , Å	9.672(3)	18.380(3)	23.180(3)
c , Å	17.880(6)	23.640(4)	16.817(2)
β , deg	103.24(2)	97.23(1)	90.84(2)
V , Å^3	2324.4(1.0)	4759.8(1.0)	5279.7(1.0)
Z	2	4	4
T , °C	24	23	24
D(calc), g cm^{-3}	1.309	1.517	1.248
μ , cm^{-1}	3.7	29.5	24.6
2θ range, deg	0 - 52	0 - 44	0 - 52
F measured	5436	6446	8952
F > 3.0 σ(F) in LS refinement	3066	4233	5034
Final R	0.036	0.043	0.044
wR	0.050	0.048	0.061
S	1.352	1.474	1.536