New Clathrate Compounds, Diamminemetal(Ni, Cu, Zn, or Cd) Tetracyanopalladate(II) and Tetracyanoplatinate(II) Aromatics Clathrates[*1]

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In previous reports,[1,2] we have discussed a series of clathrates $M(NH_3)_2Ni(CN)_4\cdot 2G$ where M is Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn or Cd, and G is benzene or aniline.

Recently we found that the use of tetracyanopalladate(II) or tetracyanoplatinate(II) in place of tetracyanoniccolate with a divalent metal salt gives similar compounds with the following formulae, $M(NH_3)_2Pd(CN)_4\cdot 2G$ and $M(NH_3)_2Pt(CN)_4\cdot 2G$ where M is Ni(II), Cu(II), Zn or Cd, and G is benzene or aniline.

These new compounds may have lamellar structures similar to those of the first mentioned series of the clathrates, $M(NH_3)_2Ni(CN)_4\cdot 2G$.

These compounds consist of "host" layers of the composition $M(NH_3)_2Ni(CN)_4$ and the "guest" aromatic molecules trapped in cavities between these sheets. In each sheet, the $Ni(CN)_4$ group has a planar structure and an octahedral configuration of ligands around M(II) is attained by four nitrogen atoms of the CN groups in plane and two ammonia molecules.

In the new series of clathrates, the position of the diamagnetic nickel atoms at the center of the square planar sites would be filled by divalent palladium or platinum. Their effective magnetic moments (μ_{eff}: Ni-Pd-Bz, 3.06; Ni-Pt-Bz, 3.10; Cu-Pd-Bz, 1.78; Cu-Pt-Bz, 1.76 B.M.) and the close resemblance of their infrared spectra to those of the clathrates, $M(NH_3)_2Ni(CN)_4\cdot 2C_6H_6$ support the present view on their structures. But the out-of-plane vibrational band ν_{11} (CH bending A_{2u} mode) due to benzene, which has been observed at 675 cm^{-1} in gaseous state and at 704—706 cm^{-1} in $M(NH_3)_2Ni(CN)_4\cdot 2C_6H_6$,[3] was found to be shifted to lower frequency side by 5 cm^{-1} in $M(NH_3)_2Pd(CN)_4\cdot 2C_6H_6$ and in $M(NH_3)_2Pt(CN)_4\cdot 2C_6H_6$.

The crystal of the benzene clathrates shown in the table with the general formulae, $M(NH_3)_2Ni(CN)_4\cdot 2C_6H_6$, $M(NH_3)_2Pd(CN)_4\cdot 2C_6H_6$ and $M(NH_3)_2Pt(CN)_4\cdot 2C_6H_6$ were all found to belong to the tetragonal system by the use of powder X-ray diffraction techniques. The lattice constants given in the table show that the clathrates in the palladium series have the largest and those in the nickel series have the smallest unit cells when M is the same divalent cation.

		a (Å)	c (Å)	ν_{11}^* (cm^{-1})
Ni-Ni-Bz	pale violet	7.24	8.28	706
Ni-Pd-Bz	pale violet	7.44	8.39	700
Ni-Pt-Bz	pale violet	7.42	8.29	702
Cu-Ni-Bz	greyish pale green	7.39	8.24	706
Cu-Pd-Bz	sky blue	7.58	8.29	699
Cu-Pt-Bz	sky blue	7.58	8.25	699
Zn-Ni-Bz**	light yellow	7.39	8.29	705
Zn-Pd-Bz**	white	7.58	8.32	700
Zn-Pt-Bz**	white	7.60	8.24	699
Cd-Ni-Bz**	light yellow	7.64	8.37	704
Cd-Pd-Bz**	white	7.77	8.38	697
Cd-Pt-Bz**	white	7.78	8.29	698
Cd-Pd-An**	white	7.81	8.65	—

* Out-of-plane CH bending band of clathrated benzene.

** Diamagnetic

The above mentioned shifts of the ν_{11} band in the infrared spectra could be correlated with the enlargement of the unit cells of the benzene clathrates in the palladium and platinum series.

Preliminary experiments have shown that the lattice $Cd(NH_3)_2Pd(CN)_4$ which has the largest lattice constants in the table can trap fluorobenzene which has, according to Hofmann and Arnoldi,[4] too large molecular volume to form a clathrate with the lattice $Ni(NH_3)_2Ni\cdot(CN)_4$.

The formation of the fluorobenzene clathrate, $Cd(NH_3)_2Pd(CN)_4\cdot nC_6H_5F$ ($n<2$) was confirmed by measuring the infrared spectra and the broad line NMR spectra of ^{19}F and proton.

[*1] The Metal Ammine Cyanide Aromatics Clathrates. III. Part II is Ref. 2.

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3) T. Miyoshi, T. Iwamoto and Y. Sasaki, *Inorg. Chim. Acta*, in press (1967).

4) K. A. Hofmann and H. Arnoldi, *Ber.*, **39**, 339 (1906).