New Clathrate Compounds, Diamminemetal (Mn, Fe, Co or Zn) Tetracyanoniccolate Dibenzene and Dianiline*1

Taku NAKANO, Tadahiko MIYOSHI, Toschitake IWAMOTO
and Yukiyoshi SASAKI

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo

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As an extention of our preparative studies of aromatics clathrates similar to those prepared by Hofmann *et al.*,1) we report here the synthesis of new compounds with a general formula, $M(NH_3)_2Ni(CN)_4 \cdot 2G$ where M is Mn(II), Fe(II), Co(II), or Zn(II) and G is benzene or aniline.

The following lamellar structure has been reported by an X-ray work for the Hofmann's benzene clathrate, $Ni(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$. Plane sheet polymers are built of diamagnetic planar $Ni(CN)_4{}^{2-}$ and paramagnetic $Ni(NH_3)_2{}^{2+}$ units, in which the nickel atoms of the both kinds are joined together by CN bridges to form nets composed of squares, and "guest" benzene molecules are trapped in cavities between such layers.2)

The paramagnetic nickel can be replaced with copper or cadmium as described in detail in our previous paper.3) The data described in the present report imply that the new compounds also have the structures identical to that of the Hofmann's clathrate, except the octahedral sites for the paramagentic nickel being occupied by other divalent metals instead. The new clathrates were obtained as fine crystals by stirring benzene or aniline with an ammoniacal solution containing potassium tetracyanoniccolate, ammonium chloride and chloride of one of the above-mentioned divalent metals. Except the compound containing zinc, all the samples were prepared and handled in a nitrogen atmosphere to prevent oxidation.

The clathrates thus obtained had approximately stoichiometric compositions corresponding to the formula $M(NH_3)_2Ni(CN)_4 \cdot 2G$, although they are not stable in an open air.

The X-ray diffraction patterns indicate that the new clathrates belong to tetragonal system. The lattice constants, *a* and *c* are given in Table 1. The infrared spectra of the clathrates were recorded and complete sets of vibrational assignment were established as has been made for other clathrates.4) In all the cases, the out-of-plane vibrational bands of the clathrated benzene were found to be shifted to higher frequency side from those of gaseous benzene. The bands due to the clathrated benzene themselves were not affected by the replacement of the metal in the octahedral sites, while the positions of ammonia and cyanide bands depend on the metal in these sites.

TABLE 1

	Color	*a* Å	*c* Å	μ_{eff} B. M.
Mn-Ni-Bz*	Greyish yellow	7.46	8.38	6.16
Fe-Ni-Bz	Greyish yellow	7.34	8.31	5.34
Co-Ni-Bz	Pink	7.36	8.34	4.88
Ni-Ni-Bz3)	Pale violet	7.24	8.28	3.20
Cu-Ni-Bz3)	Greyish pale green	7.39	8.24	1.97
Zn-Ni-Bz	Light yellow	7.39	8.29	Diamagnetic
Cd-Ni-Bz3)	Light yellow	7.64	8.37	Diamagnetic
Mn-Ni-An	Greyish yellow	(6.70)	8.93	6.51
Fe-Ni-An	Greyish yellow	7.30	9.18	5.92
Co-Ni-An	Pink	7.31	9.14	5.21
Ni-Ni-An3)	Pale violet	7.29	9.33	3.40
Cu-Ni-An3)	Dark green	**	8.81	1.98
Zn-Ni-An	Formation not confirmed			
Cd-Ni-An3)	Light yellow	7.56	8.66	Diamagnetic

* M-Ni-Bz (or An) = $M(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ (or $2C_6H_5NH_2$)

** orthorhombic or monoclinic

The manganese, iron and cobalt compounds were paramagnetic and their effective magnetic moments, μ_{eff}, show the values of their high-spin configurations.

On the Mössbauer spectrum of the iron compound, the isomer shift $\delta = 1.20$ mm/sec relative to stainless steel and the quadrupole splitting $2\varepsilon = 0.95$ mm/sec were observed. This δ value falls on the region commonly observed with typical iron(II) complexes. The rather small 2ε value suggests a good charge symmetry around the iron(II) ions.

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*1 The Matal Ammine Cyanide Aromatics Clathrates. II. Part I is Ref. 3.

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