

*Note added in proof:* After this paper was submitted, a paper (11) reported the structure of another oxygen-carrying bis(salicylaldehyde) ethylenediimine cobalt(II) compound. This compound crystallized as a dimer, the O<sub>2</sub> group bridging between the cobalt atoms, with dimethylformamide molecules occupying the sixth position around the cobalt atoms.

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#### References and Notes

1. L. Vaska, *Science* **140**, 809 (1963).
2. J. A. Ibers and S. J. LaPlaca, *ibid.* **145**, 920 (1964); S. J. LaPlaca and J. A. Ibers, *J. Amer. Chem. Soc.* **87**, 2581 (1965); J. A. McGinnety, R. J. Doedens, J. A. Ibers, *Science* **155**, 709 (1967); *Inorg. Chem.* **6**, 2243 (1967); J. A. McGinnety and J. A. Ibers, *Chem. Commun.* **1968**, 235 (1968).
3. P. Pfeiffer, E. Breith, E. Lubbe, T. Tsumaki, *Ann. Chem. Liebigs* **503**, 84 (1933).
4. A. E. Martell and M. Calvin, *Chemistry of the Metal Chelate Compounds* (Prentice-Hall, Englewood Cliffs, N.J., 1952).
5. W. P. Schaefer and R. E. Marsh, *Acta Crystallogr.* **21**, 735 (1966); R. E. Marsh and W. P. Schaefer, *ibid.* **B24**, 246 (1968); W. P. Schaefer, *Inorg. Chem.* **7**, 725 (1968).
6. C. K. Johnson, ORTEP (A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations), *Oak Ridge Nat. Lab.* 3794 (1965).
7. W. P. Schaefer and R. E. Marsh, *Acta Crystallogr.*, in press.
8. W. P. Schaefer and B.-C. Wang, abstracts of paper INOR-20, 158th national meeting, American Chemical Society, New York, 1969.
9. E. Bayer and P. Schretzman, *Struct. Bonding* **2**, 181 (1967).
10. A. Haim and W. K. Wilmarth, *J. Amer. Chem. Soc.* **83**, 509 (1961).
11. M. Calligaris, G. Nardin, L. Randaccio, *Chem. Commun.* **1969**, 763 (1969).
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## Benzene Complexes with Copper(II)montmorillonite

**Abstract.** Benzene formed a stable complex through its  $\pi$  electrons to the copper ion in copper(II)montmorillonite. Copper(II) was the only exchangeable metal cation in montmorillonite to form a complex with benzene. Only those clay minerals whose charge arises in the octahedral layer produced the complex.

The adsorption of organic molecules on clay surfaces is highly dependent on the cationic species (exchangeable cation) satisfying the negative charge site of the clay (1). Organic molecules commonly are bonded to the exchangeable cation either by formation of a complex or by hydrogen bonding. Empty *d* orbitals of certain metal ions provide coordination sites for electrons

of Lewis base organic molecules. Benzene has only electrons in  $\pi$  orbitals available for such bonding.

Benzene adsorption was studied on thin self-supporting films (2 mg of clay per square centimeter) of homoionic Wyoming montmorillonite (API No. 25) with the following exchange cations: Na, Ca, Al, Cr(III), Cu(II), Fe(II), Fe(III), Ag(I), Mn(II), Ni(II), Co(II),

and Zn. For preparation of the films, clay suspensions were dried on a flat polyethylene surface and then peeled away. The clay films were dried in a vacuum desiccator containing P<sub>2</sub>O<sub>5</sub> (24 hours) and, while still in a partial vacuum, exposed to benzene vapor over a free benzene surface for a few minutes. A period of at least another 24 hours was allowed for equilibrium to be reached. The color of the Cu(II)-montmorillonite film changed from a very pale blue to dark red within a few minutes after it was exposed to benzene. Exposing the Cu(II)montmorillonite film to room conditions caused the color to change from dark red to green or gray. The original dark red color could be restored by mild heating or desiccation, which reduced the water content of the film. The color of the films with benzene complexes was sensitive to the water content of the air. The clay films containing the other exchangeable cations showed no color change on exposure to benzene. The films were scanned in the infrared range from 600 to 4000 cm<sup>-1</sup> (Fig. 1). The broad increase in absorption between 1700 and 4000 cm<sup>-1</sup> is a striking feature of the Cu(II)-benzene-montmorillonite complex. In addition, the bands at 689, 706, 780 ± 5, 1192, 1277, 1482, and 1535 cm<sup>-1</sup> are in marked contrast to the spectrum of liquid benzene. The spectrum of benzene physically adsorbed on montmorillonite gives mainly a sharp band at 1482 cm<sup>-1</sup>. Montmorillonite saturated with the other exchangeable cations did not form complexes with benzene. This indicates that benzene was bonded to the Cu(II) cation and not to exposed silica or alumina surfaces of the montmorillonite.

Since the  $\pi$  electrons of benzene are the only ones available for bonding, we made a more detailed study of Fig. 1C to find band changes which might be associated with the  $\pi$  bonding of benzene to copper(II). An increase in the force constant of  $\nu_{11}$  (CH out-of-plane deformation) is commonly observed with dibenzenechromium(I) and dibenzenechromium (2), in both cases benzene being  $\pi$ -bonded to the metal. The  $\nu_{11}$  band increased from 675 to 795 cm<sup>-1</sup> in dibenzenechromium(I). The infrared spectrum of our Cu(II)-benzene-montmorillonite complex revealed a band at 780 ± 5 cm<sup>-1</sup> partially hidden by a band of the clay. This band is probably associated with the CH out-of-plane deformation ( $\nu_{11}$ ). The

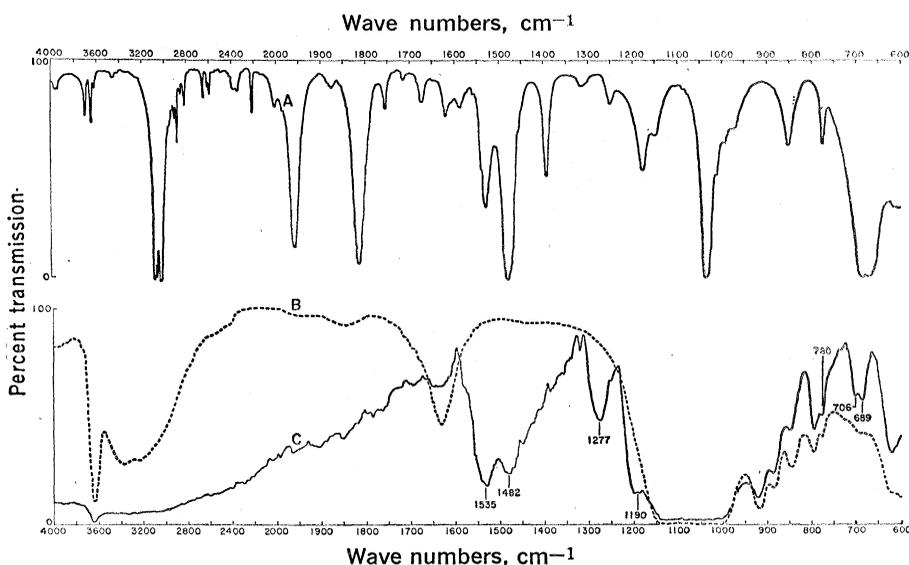


Fig. 1. Infrared spectra of (A) liquid benzene, (B) Cu(II)montmorillonite, and (C) Cu(II)-benzene-montmorillonite complex. Spectra B and C have the same base line.

Table 1. Clay minerals with Cu(II) as the exchangeable cation tested for benzene complex formation; O, source of charge in octahedral layer; T, source of charge in tetrahedral layer; +, complex formed; —, no complex formed.

Mineral	Source	API No.*	Source of negative charge	Result of benzene treatment
Montmorillonite	Wyoming	25	O	+
Montmorillonite	Arizona	23	O	+
Hectorite	California	34	O	+
Hectorite	Synthetic†		O	+
Nontronite	Washington	33A	T	—
Saponite	Scotland		T	—
Vermiculite	Montana		T	—
Beidellite	Michigan		T	—
Beidellite	Synthetic‡		T	—
Attapulgitic	Georgia	43		—
Kaolinite	Georgia	4		—

\* American Petroleum Institute, Research Project 49 (1951), Reference Clay Minerals. † Baroid Division of National Lead Co. ‡ Tem-Pres Research Inc.

bands at 689 and 706  $\text{cm}^{-1}$  were also attributed to out-of-plane CH deformation. The adsorption of benzene on various silica surfaces and zeolites increases CH out-of-plane deformation by about 10  $\text{cm}^{-1}$  and was attributed to disturbances in the benzene  $\pi$  electron system (3). In our complex, the benzene associated with the bands at 689 and 706  $\text{cm}^{-1}$  was more weakly held than that at  $780 \pm 5 \text{ cm}^{-1}$ , since exposing the clay to room conditions resulted in a loss of the former bands. Placing a freshly prepared benzene complex film in an oven at 110°C stabilized the bands at 689 and 706  $\text{cm}^{-1}$  and also stabilized the dark red color against changing to gray or green after exposure to room conditions. Studying  $\pi$  complexes of benzene with chromium, Snyder (2) found the  $\nu_{10}$  vibration at 1014  $\text{cm}^{-1}$  in  $\text{Cr}(\text{C}_6\text{H}_6)_2$  as compared with 852  $\text{cm}^{-1}$  in liquid benzene. It may be that the band at 1192  $\text{cm}^{-1}$  in the Cu(II)montmorillonite-benzene complex represents a similar shift in this CH out-of-plane deformation vibration. Other bands in this complex may also result from similar shifts. The broad band culminating at 1482  $\text{cm}^{-1}$  may have resulted from an array of C—C stretching vibrations. The band at 1535  $\text{cm}^{-1}$  corresponds to the combination band of benzene,  $\nu_{11} + \nu_{10}$ . However  $\nu_{11}$ , a vibration caused by CH out-of-plane deformation, was increased to 689, 706, and 780  $\text{cm}^{-1}$ , and  $\nu_{10}$  may have been increased to 1192  $\text{cm}^{-1}$  which would have resulted in an increased frequency for the combination band. Unlike chromium or chromium(I), copper has not been reported to make the "sandwich" complexes with benzene. Turner and Amma (4) reported the structural details of  $\text{C}_6\text{H}_6 \cdot \text{CuAlCl}_4$  by three-dimensional

Fourier analysis. According to them, the benzene molecule was bonded through an edge C—C group to the cuprous ion. This resulted in essentially two classes of C—C bond lengths, one of 1.40 Å, close to that of benzene, and the other of about 1.27 Å, between that of a double and triple C—C bond. Perhaps interruption of bond resonance in the benzene ring may have occurred, and the band at 1535  $\text{cm}^{-1}$  may result from a C—C stretching frequency of primarily double bond character while that at 1277  $\text{cm}^{-1}$  may represent a C—C stretching from predominately single bonds. We tested benzene complex formation with Cu(I)montmorillonite with positive results, finding an identical spectrum to that of Cu(II)montmorillonite. The oxidation status of the exchangeable copper ions is thus in question.

Freeze-dried Cu(II)montmorillonite was treated with benzene vapor to form the complex which was then soaked 24 hours in liquid benzene at normal atmospheric pressure in a desiccator over  $\text{P}_2\text{O}_5$ . This resulted in a very dark red clay. Excess benzene was then removed by evaporation and the complex was degassed for 2 hours; during this time the film changed to lighter red. At this stage total carbon determined by combustion showed a 4 : 1 molar ratio of Cu(II) to benzene. The intensity of the red color is undoubtedly related directly to the amount of benzene in the complex, thus, some benzene must have been lost during degassing.

Toluene, xylene, and chlorobenzene also formed complexes with Cu(II)montmorillonite. Again, no complex formed when the exchangeable cations were Co(II), Ca, Ni(II), Zn, or Fe(III). Toluene gave a bright green complex

with Cu(II)montmorillonite, xylene a dark purple complex, and chlorobenzene a dark red to green complex.

We decided to repeat the above experiment with benzene for several other clays with Cu(II) as the exchangeable cation. Of the clays tested, only those in which the negative charge arises from isomorphous substitution in the octahedral layer formed complexes with benzene (Table 1). Suspecting that hydration differences between the Cu(II)-saturated clays were responsible for this observation, we washed several of the tetrahedrally charged clays with methanol to remove coordinated water, dried them over  $\text{P}_2\text{O}_5$  in a vacuum, and exposed them to benzene vapors. No complexes were observed, but water was still present as judged from infrared absorption. This suggests important differences in the hydration properties of Cu(II)-swelling clays, the tetrahedrally charged varieties being much more stable.

The formation of benzene complexes with Cu(II)montmorillonite and the resulting possible disruption of the bond resonance in benzene suggest important new pathways for synthesis via the complex. The clay itself must be a stabilizing factor in preserving this complex since aromatic compound-metal complexes commonly decompose when exposed to the air. The ability of Cu(II)-saturated, octahedrally charged, swelling clays to form a complex may provide a quick method of determining the site of the negative charge in montmorillonites.

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#### References and Notes

1. M. M. Mortland and W. F. Meggitt, *Agr. Food Chem.* **14**, 126 (1966); R. H. Dowdy and M. M. Mortland, *Clays Clay Minerals* **15**, 259 (1967); H. E. Doner and M. M. Mortland, *Clays Clay Minerals*, in press.
2. H. Saito, Y. Kakiuti, M. Tstutsui, *Spectrochim. Acta* **15**, 807 (1959); R. G. Snyder, *ibid.*, p. 807.
3. G. A. Galkin, A. V. Kiselev, V. I. Lygin, *Trans. Faraday Soc.* **60**, 431 (1964); V. N. Abramov, A. V. Kiselev, V. I. Lygin, *Zh. Fiz. Khim.* **37**, 1156 (1963); S. A. Galkin, A. V. Kiselev, V. I. Lygin, *ibid.* **36**, 1764 (1962); C. I. Angell and M. V. Howell, *J. Coll. Interface Sci.* **28**, 279 (1968).
4. R. W. Turner and E. L. Amma, *J. Amer. Chem. Soc.* **88**, 1877 (1966).
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