incorporated 4-AP. Their oxygen atoms replace chloride ions in the interlayer surface of FeOCl as in the case of FeOOCH$_3$, but half of the grafted EG molecules are chelated to ferric ions within the same layer plane.

Notes

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Immediate Formation of a Layered Compound, FeOOCH$_3$, by a Topochemical Reaction

S. Son, S. Kikkawa, F. Kanamaru, and M. Koizumi*

We have recently reported that FeOOCH$_3$, a new layered compound, whose structure can be derived from γ-FeOOH or FeOCl by replacing OH or Cl with CH$_3$O, was prepared by soaking an intercalated compound, FeOCl(4-AP)$_{1/4}$, where 4-AP indicates 4-aminopyridine, in methanol at 110 °C for 6 days.[1] In this case the reaction was expressed by

$$FeOCl(4\text{-}AP)_{1/4} + CH_3OH \rightarrow FeOOCH_3 + HCl + 4\text{-}AP$$
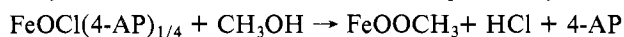
This new compound, FeOOCH$_3$, could not be obtained by direct reaction between FeOCl and methanol in a temperature range from room temperature to 110 °C. However, we have found quite a simple method to prepare FeOOCH$_3$ by the direct reaction of FeOCl with sodium methoxide. In this paper, the preparation and some properties of FeOOCH$_3$ are presented.

Experimental Section

Preparation of FeOCl was carried out by the same method published previously.[1] The thin, bladelike FeOCl crystals were crushed to powder form before use as a host material. Sodium methoxide (28% in methanol) used here was purchased from Nakarai Chemicals Ltd. About 3 mmol of FeOCl and 1 mL of sodium methoxide were put into a 20-mL heavy-walled Pyrex tube equipped with a screw cap, and the mixture was allowed to warm at 60 °C. Upon being warmed, the vessel was placed in a water bath with occasional shaking at 60 °C for 10 h to ensure complete reaction. The product was separated from the solution by filtration, washed with methanol and then with water to remove NaCl which was produced by subreaction, and finally dried under vacuum.

X-ray analysis was carried out with a Rigaku-Denki diffractometer using Cu Kα radiation. Chemical analysis of the complex was made by using standard techniques. Differential thermogravimetric analysis was made by using a Rigaku-Denki unit programmed for a heating rate of 10 °C/min. The infrared spectra in the region 4000–700 cm^{-1} were obtained on a Hitachi Perkin-Elmer spectrophotometer fitted with a sodium chloride prism. Samples were dispersed in potassium bromide disks. Calibration of the spectrophotometer was made by using polystyrene bands.

Results and Discussion

After the complete reaction of FeOCl and CH$_3$ONa, FeOCl changed from reddish violet to brown. The quite same phenomenon was observed for the compound prepared by the previous method.[1] The product was stable in air for a long period of time. The compound was identified to be FeOOCH$_3$

by chemical, IR, X-ray diffraction, and differential thermogravimetric analyses as described below. Anal. Calcd for FeOOCH$_3$: C, 11.7; H, 2.94; Cl, 0.00. Found: C, 9.26; H, 2.33; Cl, 0.00. The reaction to give FeOOCH$_3$ from CH$_3$ONa and FeOCl is

$$FeOCl + CH_3ONa \rightarrow FeOOCH_3 + NaCl$$
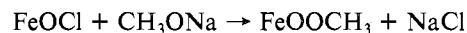
The presence of NaCl was recognized by X-ray diffraction of the product before washing. During the reaction, no coloring in solution and no changing in shape were recognized. These facts suggest that the reaction might have proceeded topotaxially; that is, FeOOCH$_3$ was produced by the interlayer substitution of CH$_3$O for Cl of FeOCl, remaining the iron and oxygen double layers of FeOCl. From X-ray diffraction, it was found that the compound had the basal spacing of 10 Å which is about 2 Å larger than that of FeOCl, and the X-ray powder diffraction data were superposed on previous data.[1] In the infrared spectrum of FeOOCH$_3$, a strong band at 1050 cm^{-1} assigned to the stretching vibration of the C–O bond was found. Thermal analysis data of FeOOCH$_3$ showed that the compound decomposed at 300 °C associated with 19% weight loss. The sample cooled from 350 °C was identified to be γ-Fe$_2$O$_3$ by X-ray diffractometry. These results indicate that FeOOCH$_3$ prepared by the present method is not a sorption-type complex but a layered-type compound with a strong bonding between the CH$_3$O and the inorganic layers.

We also attempted to prepare VOOCH$_3$ from VOCl and CH$_3$ONa by the present method, but the desired compound could not be prepared. VOCl[2] has a crystal structure similar to that of FeOCl, and both compounds intercalate pyridine molecules. This phenomenon is very difficult to explain, but it is interesting for us to investigate why VOOCH$_3$ was not obtained and the mechanism of substitutional reaction between Cl and CH$_3$O in the interlayer region.

(2) M. C. Levayer and M. J. Rouxel, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **268**, 167 (1969).

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Spectroscopic Characterization of Tetrakis(pyridine)copper(II) Complexes in Zeolite Y

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Adsorbed pyridine (py) reacts with copper ions in both X- and Y-type zeolites, forming a complex which has been identified on the basis of its EPR spectrum as [Cu^{II}(py)$_4$]$^{2+}$.[1–4]

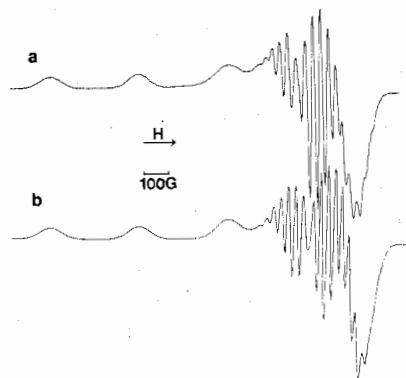(1) S. Kikkawa, F. Kanamaru, and M. Koizumi, *Inorg. Chem.*, **15**, 2195 (1976).

Figure 1. EPR spectrum of $[Cu^{II}(py)_4]^{2+}$ complex in zeolite Y: (a) experimental; (b) simulated.

Figure 2. Intensity of the $[Cu^{II}(py)_4]^{2+}$ EPR spectrum vs. the molecules of py adsorbed per Cu^{2+} ion: ●, intensity based on $m_I = -^3/_2$ component of the spectrum; ▲, intensity based on the high-field minimum.

In addition to g values, the spectrum is characterized by only copper hyperfine splitting in the low-field region and by a large number of overlapping hyperfine and superhyperfine lines in the high-field region of the spectrum. The spectrum is consistent with that expected for the tetrapyridine complex; however, a degree of ambiguity remains in the assignment since no attempt has been made to simulate the spectrum by assuming a smaller number of ligands. Recently, we have synthesized a $[Cu^{II}bpy]^{2+}$ (bpy = bipyridine) complex in a zeolite Y, and it has more than 12 resolvable lines in the high-field region of the spectrum.[6] Moreover, the maximum dimension of the $[Cu^{II}(py)_4]^{2+}$ complex (12.0 Å)[5] is approaching the diameter (13 Å) of the large cavities in the faujasite-type structures.

Because $[Cu^{II}(py)_4]^{2+}$ has been cited as an example of an *intra*-zeolitic transition-metal complex which is formed by the migration of a copper ion from a relatively hidden site to one in the large cavity, it was of interest to further study the identity of the complex. In the work reported here EPR spectroscopy and diffuse reflectance spectroscopy have been combined with gravimetric experiments to confirm the identification of the tetrapyridine complex. In addition, simulated EPR spectra establish that a model involving four pyridine molecules provides the best fit with the experimental spectrum. Ancillary information has been gained on the ease of oxidation and reduction of the complexed copper ions.

Zeolite-Y samples, originally in the sodium form, were exchanged in 0.02 N $Cu(NO_3)_2$ to levels of 1.8 and 18 Cu^{2+} ions per unit cell. Standard pretreatment included heating the samples under vacuum to 400 °C in increments of 100 °C/h. The samples were then exposed to 350 torr of O_2 for 1 h at 350 °C, and the gas phase was subsequently evacuated at that temperature. For the EPR experiments pyridine was admitted in a stepwise manner by using doses equivalent to ca. 1.0 molecule of py/Cu^{2+}, and a decrease in pressure indicated that essentially all of the pyridine was adsorbed. The sample was allowed to equilibrate for 3 h at 100 °C, and then 200 torr of O_2 was added to reoxidize any copper that was reduced by the pyridine. The O_2 was evacuated at 100 °C.

EPR spectra were recorded with the sample at –196 °C by using a Varian E6S spectrometer. The g values were measured relative to 2,2′-diphenyl-1-picrylhydrazyl (DPPH) standard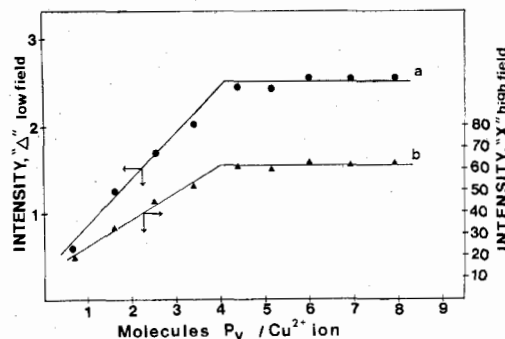 with g = 2.0036. Spin concentrations were calculated by numerical double integration of the derivative spectra. The standard for spin-concentration determinations was phosphorus-doped silicon. The uncertainty in the spin-concentration determination is estimated to be ±30%. Simulated EPR spectra were calculated by using the computer program SIM 13.

The EPR spectrum of the dehydrated $Cu_{1.8}Na$–Y sample was characterized by $g_\parallel^1$ = 2.38 and $g_\parallel^2$ = 2.30 with $|A_\parallel^1|$ = 108 G and $|A_\parallel^2|$ = 175 G, which is in agreement with previously reported spectra.[7] Upon adsorption of pyridine vapor at 100 °C, this spectrum decreased in intensity and the spectrum of the Cu(II)–py complex, depicted in Figure 1a, grew in intensity. Ultimately both types of copper ions in the dehydrated zeolite became coordinated to the pyridine, forming a single type of complex. The spectrum of the complex has been simulated, by assuming either two or four equivalent nitrogen nuclei bonded to a Cu^{2+} ion. Only with four nitrogen nuclei was a comparable spectrum obtained. The EPR spectrum of Figure 1b was simulated by using $|A_\perp^{Cu}|$ = 35 G, $|A_\parallel^{Cu}|$ = 183 G, $|A_\perp^N|$ = 15.08 G, and $|A_\parallel^N|$ = 9 G with $g_\parallel$ = 2.2407 and $g_\perp$ = 2.0420. Since no nitrogen hyperfine splitting was observed in the parallel direction, the value of $|A_\parallel^N|$ is not highly accurate. The simulated parameters differ from the previously reported values mainly with respect to $|A_\perp^{Cu}|$ which has been reported to be 16–17 G.[2–4]

Upon heating the $Cu_{1.8}Na$–Y sample with adsorbed pyridine to 100 °C for several hours, we observed a decrease in intensity of the Cu^{2+} signal which indicates a reduction of copper to Cu^+. The intensity of the EPR signal was completely restored by heating the sample at 100 °C in 200 torr of O_2 for 3 h. Similarly, degassing the Cu^{II}–py sample at temperatures up to 200 °C resulted in a decrease in signal intensity, but apart from smaller line widths the magnetic parameters remained the same. Thus, unlike the situation with NH_3,[8] a tetrahedral complex was not formed by the loss of three pyridine ligands.

With use of a technique described by Flentge et al.[9] the amplitude of the EPR spectrum was determined as a function of the pyridine adsorbed in the zeolite. The product of the peak height times the square of the width at half-maximum, denoted by Δ, was determined for the low-field hyperfine component, and the results are plotted in Figure 2a. Likewise the amplitude of the minimum in the high-field region, denoted by X, is plotted in Figure 2b as a function of the py/Cu^{2+} ratio. The important feature of these two curves is the inflection point which occurred at a py/Cu^{2+} ratio of 4, and thereafter the number of complexes did not increase with the addition of more pyridine.

(1) J. R. Leith and H. F. Leach, *Proc. R. Soc. London, Ser. A*, **330**, 247 (1972).
(2) C. Naccache and Y. Ben Taarit, *Chem. Phys. Lett.*, **11**, 11 (1971).
(3) J. Turkevich, Y. Ono, and J. Soria, *J. Catal.*, **25**, 44 (1972).
(4) J. C. Vedrine, E. G. Derouane, and Y. Ben Taarit, *J. Phys. Chem.*, **78**, 531 (1974).
(5) A. H. Levin, *Chem. Commun.*, **21**, 1400 (1971).
(6) J. H. Lunsford and W. DeWilde, *Inorg. Chim. Acta*, **34**, L229 (1979).

(7) R. G. Herman and D. R. Flentge, *J. Phys. Chem.*, **82**, 720 (1978).
(8) E. F. Vansant and J. H. Lunsford, *J. Phys. Chem.*, **76**, 2860 (1972).
(9) D. R. Flentge, J. H. Lunsford, P. A. Jacobs, and J. B. Uytterhoeven, *J. Phys. Chem.*, **79**, 354 (1975).

Table I. Spin Concentration of $Cu_{1.8}$Na-Y upon Addition of Pyridine at 100 °C

py molecules ads/Cu^{2+}	spin concn × 10^{-20}, spins/g of ZY^b	mol of Cu^{2+}/ g of ZY^b × 10^4
0	6.2	1.0·(1.4)^a
0.72	7.1	1.2
1.60	6.3	1.0
2.50	7.1	1.2
3.40	7.0	1.1
4.28	7.1	1.2
5.16	6.8	1.1
6.06	7.1	1.2
6.94	7.1	1.2
7.92	7.2	1.2

^{a} Obtained from chemical analysis. ^{b} ZY = zeolite Y.

Table I shows that the total Cu^{2+} concentration remained constant upon the stepwise addition of pyridine, under the conditions described previously, and, furthermore, within experimental error the Cu(II) detected by EPR was equivalent to the total amount of copper in the sample. These results establish that the stoichiometry suggested by Figure 2 was not in error due to the presence of a large concentration of Cu^+. Furthermore, together with the EPR data they confirm that all of the Cu^{2+} ions participated in complex formation when a stoichiometric amount of pyridine was present.

Additional evidence for the formation of the $[Cu^{II}(py)_4]^{2+}$ complex comes from the diffuse reflectance spectra which were obtained by using a Cary 14 R spectrophotometer with a Type II reflectance attachment. The spectrum of Cu_{18}Na–Y after dehydration at 400 °C had a band maximum at 10 800 cm^{-1} and a shoulder around 14 300 cm^{-1}. Adsorption of pyridine at 100 °C resulted in the disappearance of these bands and the formation of an intense new band at 17 300 cm^{-1}. This spectrum is in excellent agreement with the single-crystal spectrum of $[Cu/Cd(C_5H_5N)_4]S_2O_8$, for which a band at 17 200 cm^{-1} was assigned to the $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2B_{2g}$ transitions.[10]

Clearly the results described here confirm the earlier assignment of the Cu^{II}–py complex as $[Cu^{II}(py)_4]^{2+}$. The free energy of formation must strongly favor this complex since there is no evidence for complexes in the zeolite which contained less than four ligands, in contrast to the Cu^{II}–ethylenediamine case for which mono, bis, and tris complexes were observed.[11] Furthermore, the results depicted in Figure 2 reveal that the copper ions compete very favorably with the zeolite for ligands.

The question of charge compensation by the Cu^{2+} ion in the complex, which may be far removed from the oxide ions of the lattice, has been addressed by Gallezot et al.[12] These authors suggest that the formation of the organometallic complex is accompanied by a proton transfer to the framework oxygen atoms, which they believe is necessary to neutralize the negative charge on the zeolite. More recently Maes and Cremers[13] have suggested that the enhanced stabilization of similar complexes, particularly in layer-lattice clays, may be due to a charge delocalization over the ligands. Such may be the case for $[Cu^{II}(py)_4]^{2+}$ complexes in zeolites; however, one might expect that charge delocalization would be accompanied by a change in nitrogen spin density. When this parameter is compared for the complex in the zeolite and in solution,[14]

it is evident that the difference in calculated spin densities is less than 5%.

(14) E. G. Derouane, J. N. Braham, and R. Hubin, *Chem. Phys. Lett.*, **25**, 243 (1974).

X-ray Photoelectron Spectra of Copper(III) Complexes

Dennis G. Brown* and Ulrich Weser

We have recently reported the X-ray photoelectron spectrum of a number of metal–biureto complexes, one of which was a copper(III) system.[1] The spectrum of this species, potassium bis(biureto)cuprate(III), $KCu(bi)_2$, exhibited a rather intense satellite at high binding energy from the Cu 2p main peaks. Another recent report of the XPS of a copper(III) macrocycle has indicated no satellite structure in this region.[2] To our knowledge these are the only two reports of XPS for copper(III).[3] Because of the different behavior exhibited by these two copper(III) systems, it was of interest to us to prepare additional stable copper(III) compounds which might provide more information about the X-ray photoelectron spectral properties of copper(III). We report here the XPS of two additional copper(III) complexes, along with the spectra of the corresponding copper(II) systems. The spectra of both copper(III) complexes exhibit satellites to the high binding energy side of the $2p_{1/2}$ and $2p_{3/2}$ main peaks.

For the more common oxidation states of copper it is generally agreed that copper(II) will demonstrate satellite structure in the 2p spectral region (except possibly with certain sulfur donor ligands[4,5]), while copper(I) will show no satellite structure. Earlier papers attributed the presence or absence of satellite structure in transition-metal XPS directly to the presence or absence of unpaired electrons in the complex. If this were the case, one would expect no satellite structure in the copper(III) complexes, which are low-spin d^8 systems and therefore diamagnetic. On the other hand, theoretical attempts to explain the satellite structure in transition-metal systems, especially copper(II), have invoked a charge-transfer mechanism which leads to satellite states.[6] In this case the criterion for the possibility of observing satellite structure is the presence of a partially filled (or empty) d shell, although this does not apparently necessitate the presence of a satellite of observable intensity. Within this framework the possibility of observing satellite structure in copper(III) would certainly exist.

The XPS reported here are for copper(III) and copper(II) with ligand systems derived from the condensation of biuret with ethylenediamine or *o*-phenylenediamine. The compounds have been reported previously.[7] We have prepared salts with either potassium or tetra-*n*-butylammonium cations. Figure

(10) H. G. Hecht, R. C. Kerns, and J. P. Frazier III, *J. Inorg. Nucl. Chem.*, **31**, 1983 (1969).
(11) P. Peigner, J. H. Lunsford, W. DeWilde, and R. A. Schoonheydt, *J. Phys. Chem.*, **81**, 1179 (1977).
(12) P. Gallezot, Y. Ben Taarit, and B. Imelik, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **272**, 261 (1971); *J. Catal.*, **26**, 295 (1972).
(13) A. Maes and A. Cremers, submitted for publication in *J. Chem. Soc. Faraday Trans.*

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