Infrared Study of Copper(I) Carbonyls in Y Zeolite

Yun-yang Huang*

Contribution from the Department of Chemistry, Texas A & M University, College Station, Texas 77843.

Received April 12, 1973

Abstract: Formation of carbonyl complexes in a Cu(I)Y zeolite was studied by means of infrared spectroscopy. The sample was prepared by the reduction of a 75% exchanged Cu(II)Y zeolite with carbon monoxide. The reduced sample showed an intense infrared absorption band at 2160 cm^{-1} when carbon monoxide was adsorbed at 40 Torr pressure. The band remained even after the gas had been pumped off at 25°. With ammonia preadsorbed at 25° and at 10 Torr, the CO absorption band shifted to 2080 cm^{-1}, and it disappeared on pumping. If ethylenediamine had been adsorbed at 25° and then the sample was evacuated for 3 hr, two bands at 1916 and 2090 cm^{-1} were observed; the one with lower frequency was attributed to bridging carbonyl groups and it disappeared after more ethylenediamine was desorbed at 200°. Adsorption with pyridine at 25° followed by desorption at 120° gave rise to a band at 2120 cm^{-1}. In all cases, the absorption bands shifted back to higher frequencies after the desorption of amines at higher temperatures. The shift in C–O stretching frequencies, when amines are present, is explained in terms of the change in locations of the carbonyl complexes in zeolite.

Zeolites provide a good system for studying various properties of metal ions. For instance, the faujasite type zeolites consist of three types of cages built from SiO_4 and AlO_4 tetrahedra. The supercage has a diameter of about 13 Å with free openings of about 8–9 Å. It is the location where large molecules are adsorbed and where many catalytic reactions take place. The second type is the sodalite cage, which leads to the supercage through the hexagonal window of 2.2 Å in free diameter. The sodalite cage has a diameter of about 6.6 Å. The third type is the hexagonal prism which is even smaller. The last two types of cages, to be called small cavities, are often the favorable locations for many cations, which compensate for the negative electrostatic charges introduced by Al^{3+} ions in the AlO_4 tetrahedra. These cations can be ion exchanged by others and in different proportions. The sites of the cations, their influence on the adsorption properties, and the role which they play in catalysis are of great significance in zeolite research.

Formation of transition metal complexes in zeolites has been an interesting area of investigation. In particular, copper(II) complexes have been studied in great detail by means of electron spin resonance spectroscopy.[1] The copper content of the zeolites in these studies is usually quite low, in order to avoid spin exchange interaction occurring at higher copper concentrations. Esr studies[2] show that copper(II) ammines are formed in the supercages of Y-type zeolites and four ammonia molecules are coordinated to a Cu^{2+} ion when ammonia is adsorbed at 25°. Partial desorption of ammonia at 100° changes the location and the coordination of the Cu^{2+} ions, which are surrounded by one ammonia and three oxide ions of the zeolite framework in a tetrahedral manner. Results of adsorption–desorption measurements by Huang and Vansant[3] on Y zeolites with higher copper contents give quantitative information about the cupric ammines. An X-ray diffraction study by Gallezot, Ben Taarit, and Imelik[4] shows that Cu^{2+} ions in dehydrated Cu(II)Y samples are located inside the small cavities. This means that, at sufficiently high vapor pressures of ammonia, migration of Cu^{2+} ions from the small cavities to the supercages occurs during the complex formation.

Copper(II) ions in Y zeolites can be reduced to the monovalent state by treating the sample with carbon monoxide at high temperatures. The reduction process is enhanced in the presence of ammonia,[3] which causes Cu^{2+} ions to move out of the small cavities. Only 1 hr is sufficient to convert Cu(II)Y to Cu(I)Y samples at 400°. Without preadsorbed ammonia, as long as 30 hr are required. This is an important method for preparing Cu(I) zeolites. The usual ion-exchange procedure cannot be used because cuprous solutions are relatively unstable; the Cu^+ ions are readily oxidized in the presence of air or oxygen and they would also tend to disproportionate into Cu^{2+} and Cu^0. The Cu(I)Y zeolites prepared by the above method offer a good system for studying the Cu^+ ions and their complexes. This paper presents the results of an infrared study of cuprous carbonyl complexes in Y zeolite, with or without the presence of other ligands such as ammonia, ethylenediamine, or pyridine. The adsorption study of carbon monoxide, ammonia, and other gases has recently been reported.[5]

Experimental Section

Carbon monoxide, CP grade with 95.5% purity, from Matheson Gas Products, was passed through a liquid nitrogen cold trap before use. Anhydrous ammonia, 99.99% purity, also from Matheson, was condensed in a liquid nitrogen cold trap and distilled into a gas storage bulb. Pyridine, analyzed reagent from Matheson Coleman and Bell, was taken from a fresh bottle without further purification. Ethylenediamine, 98% purity from Mallinckrodt Chemical Works, was first stirred with potassium hydroxide pellets and then stirred and refluxed with calcium hydride to remove traces of water before distillation.

Cu(I)Y zeolite was prepared *in situ* by the reduction of Cu(II)Y sample, which had 75% exchanged Cu^{2+} ions.[3] The reduction was carried out at 400° in 200 Torr of carbon monoxide and about 15 Torr of ammonia. Initially, the cupric sample was pressed into a thin pellet of thickness ranging from 9 to 17 mg/cm^2 and was placed in an infrared cell designed for the gas adsorption study. The detail of the pretreatment of the sample has been described elsewhere.[5] In the adsorption study, all gas or vapor was adsorbed at 25°.

---

* Address correspondence to author at Division of Tribophysics, CSIRO, University of Melbourne, Parkville, Victoria 3052, Australia.

(1) J. H. Lunsford, *Advan. Catal. Relat. Subj.*, **22**, 265 (1972).

(2) E. F. Vansant and J. H. Lunsford, *J. Phys. Chem.*, **76**, 2860 (1972).

(3) Y. Y. Huang and E. F. Vansant, *J. Phys. Chem.*, **77**, 663 (1973).

(4) P. Gallezot, Y. Ben Taarit, and B. Imelik, *J. Catal.*, **26**, 295 (1972).

(5) Y. Huang, *J. Catal.*, **30**, 187 (1973).

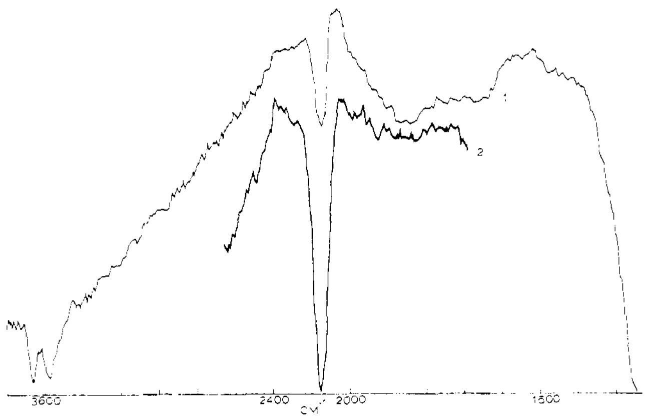

Figure 1. Infrared spectra of CO adsorbed in Cu(I)Y (75%) zeolite: (1) freshly prepared sample; (2) with the addition of 40 Torr of CO at 25°.

The infrared cell for gas adsorption study was similar to that used by Chao and Lunsford.[6] Sodium chloride windows were used. Infrared spectra were recorded at 25° by a Beckman IR 12 spectrophotometer. To investigate the carbonyl complexes, carbon monoxide was admitted to the cell at pressures below 50 Torr.

Results

After the reduction of Cu(II)Y which had a light green color, the zeolite sample turned white. An infrared spectrum between 1200 and 4000 cm^{-1} is shown in Figure 1. For the zeolite lattice, there was almost no transmission below 1200 cm^{-1}. Two absorption bands at 3560 and 3650 cm^{-1} were due to hydroxyl groups present in the Cu(I)Y zeolite. The residual carbon monoxide adsorbed in the sample gave rise to a small band at 2140 cm^{-1}. It is attributed to the Cu^{+}–CO complex. When carbon monoxide was adsorbed at 25° and 40 Torr, an intense absorption band appeared at 2160 cm^{-1}, as indicated previously.[5] The band remained practically unchanged after the gaseous carbon monoxide had been pumped off and the sample had been evacuated for 10 min.

If ammonia had been adsorbed in the Cu(I)Y sample at 25° and at 10 Torr before 40 Torr of carbon monoxide was introduced, the C–O stretching frequency then shifted to 2080 cm^{-1} (Figure 2). The absorption band almost disappeared when carbon monoxide was pumped off and the sample was evacuated for 5 min. Upon admission of carbon monoxide following the evacuation of the sample at 25° for 2 hr, the peak moved to 2125 cm^{-1} with a shoulder at 2080 cm^{-1}. A peak at 2150 and a shoulder at 2135 cm^{-1} were observed if the sample had been evacuated at 120° for 2 hr and then exposed to carbon monoxide. The major band remained after the sample had been pumped for 5 min.

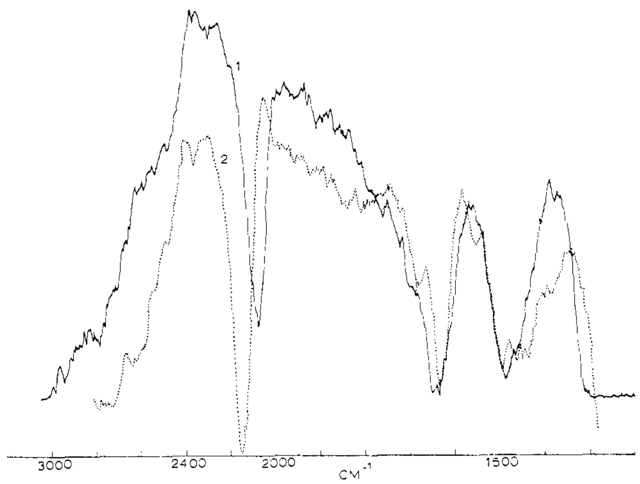

Figure 2. Infrared spectra of CO adsorbed (25°, 40 Torr) in Cu(I)Y (75%) zeolite with ammonia present: (1) 10 Torr of ammonia is adsorbed at 25°; (2) after desorption at 120°.

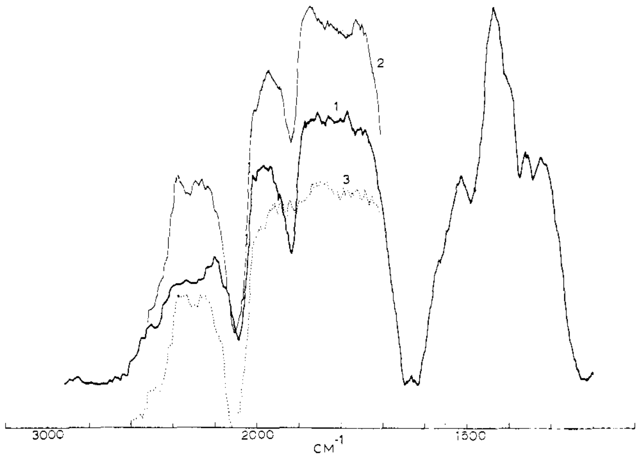

Figure 3. Infrared spectra of CO adsorbed (25°, 40 Torr) in Cu(I)Y (75%) zeolite with ethylenediamine present: (1) after desorption at 25°; (2) after desorption at 120°; (3) after desorption at 200°.

No distinguishable CO band was observed when carbon monoxide was added to Cu(I)Y zeolite which had been preadsorbed with ethylenediamine at 25° and at 10 Torr. However, if part of the adsorbed amine was removed by evacuating the sample at 25° for 3 hr, two bands at 1916 and 2090 cm^{-1} were recorded upon the addition of carbon monoxide (Figure 3). Both could be removed readily by pumping. The band at 1916 cm^{-1} became smaller, compared to that at 2090 cm^{-1}, after the sample had been evacuated at 120° for 2 hr and then 50 Torr of carbon monoxide was added. The lower frequency band did not appear after more ethylenediamine had been desorbed at 200° for 2 hr; the higher frequency band shifted to 2120 cm^{-1}. An intense band at 2150 cm^{-1} showed up after desorption at 300° for 3 hr. Absorption bands due to ethylenediamine were still observed at this stage. Also, the pellet had turned reddish brown, indicating the formation of some metallic copper from disproportionation. The CO band finally shifted to 2170 cm^{-1} after evacuation at 400°, and the intensity was considerably smaller than that recorded from a fresh sample.

The white sample turned yellow after 10 Torr of pyridine had been adsorbed at 25°. No distinct CO absorption band was observed with the addition of carbon monoxide. A broad diffuse band having a peak at 2130 cm^{-1} and a shoulder at 2190 cm^{-1} appeared after the sample had been evacuated at 25° for 7 hr and then exposed to CO. But a sharp and more intense band at 2120 cm^{-1} appeared after the desorption at 120° for 1.5 hr (Figure 4). The band shifted to 2140 cm^{-1} and then to 2155 cm^{-1} after evacuation at 300° for 3 hr and at 400° for 1.5 hr, respectively.

---

(6) C. C. Chao and J. H. Lunsford, *J. Amer. Chem. Soc.*, **93**, 71 (1971).

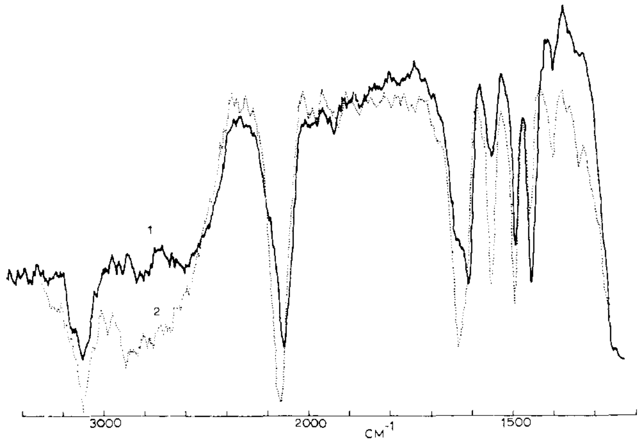

Figure 4. Infrared spectra of CO adsorbed (25°, 40 Torr) in Cu(I)Y (75%) zeolite with pyridine present: (1) after desorption at 120°; (2) after desorption at 300°.

Table I. Infrared C–O Stretching Frequencies of Copper(I) Carbonyls

Compound or medium	C–O frequency, cm^{-1}	Ref
Copper(I) trifluoroacetate carbonyl–trifluoroacetic acid	2155	9
Cu(CO)Cl in water	2112	10
Cu(CO)Cl in pyridine	2069	10
Cu(CO)Cl in methanol	2090	11
[Cu(en)(CO)]Cl	2080	11
[(en)Cu(CO)$_2$Cu(en)]Cl$_2$	1905	11
[Cu(CO)Cl(Me$_2$N=CH$_2$)]Br	2080	12
Cu(I)Y (75%) zeolite		Present work
Dehydrated	2160	
Preadsorbed with NH$_3$	2080	
Preadsorbed with en	1916, 2090	
Preadsorbed with py	2120	

Discussion

The infrared study confirms the results of the adsorption measurements about the formation of Cu$^+$–CO complexes in zeolites. The intensity of the CO absorption bands is considerably stronger than that reported in other cation-exchanged zeolites. In addition, the present work indicates that the C–O stretching frequency is significantly lowered when ammonia, ethylenediamine, or pyridine is preadsorbed in the Cu(I)Y sample.

Adsorption measurements show that at temperatures between 0 and 100° and at 100 Torr pressure of carbon monoxide is selectively adsorbed in Cu(I)Y zeolites with a limiting value of CO/Cu$^+$ close to one.[5] For the Cu(I)Y (75%) sample, there is 1.60 mmol of Cu$^+$ per gram. At 0° and at 50 Torr, the original Cu(II)Y sample adsorbs less than 0.2 mmol of carbon monoxide per gram, which is very close to that taken by NaY zeolite.[3] Zeolites having bivalent cations exposed to the supercages of the faujasite framework are known to adsorb carbon monoxide specifically, mainly due to the electrostatic interactions.[7] However, both the amount and the heat of adsorption are smaller than those of the Cu(I)Y sample.[5]

The formation of cuprous carbonyls in solutions and in coordination compounds has been reported, although only in rather limited cases.[8–15] Similar to that observed in zeolites, the limiting ratios of CO/Cu$^+$ are generally close to one. Infrared absorption frequencies of the carbonyls have also been indicated in a few instances.[11–14] They are summarized in Table I, together with the present work on zeolites. It can be seen that the carbonyl complexes in Cu(I)Y zeolite resemble those observed in solutions and in coordination compounds.

The CO stretching frequencies higher than 2143 cm^{-1} are common for carbon monoxide adsorbed on solid surfaces, metal, or metal oxides.[16] In particular, absorption bands near 2200 cm^{-1} have been observed for CO adsorbed on X and Y zeolites containing bivalent cations.[17] The origin of the high frequency bands was explained in terms of the electrostatic interaction with the cations. But carbon monoxide was considered to be weakly adsorbed in these samples. As summarized by Little,[16] several assignments have been made to interpret the bands that appear between 2140 and 2200 cm^{-1} for adsorbed CO. These include the asymmetric stretching mode for a species $\mathrm{M\cdots O\overset{\cdots}{-}C\overset{\cdots}{-}O}$, the stretching mode for an ionized species such as CO$^+$ or CO^{2+}, a stretching mode in an ion-dipole model, the CO stretch in physically adsorbed carbon monoxide, and a CO stretching mode for a σ complex involving the carbon lone-pair electrons. So far, no definite conclusion has been reached.

The present work would suggest that the σ complex due to the carbon lone-pair electrons could be responsible for the high C–O stretching frequency in the case of Cu(I)Y zeolite. The shift to lower frequencies when other ligands are present gives a clearer picture about the carbonyl complexes. The unusual stability of metal carbonyls is normally considered as due to the mutual strengthening of the σ and the π bonds between metal and carbon monoxide. Because of the back donation from metal to CO, the M–C bond is strengthened and the C–O bond becomes weaker. Thus, a lower C–O stretching frequency is usually observed in metal carbonyls. In the absence of the metal to CO back-bonding, such as that of borane carbonyl, a higher frequency than 2143 cm^{-1} would be observed. The infrared band was reported to be at 2164 cm^{-1} in this case.[18]

Adsorption measurements indicate that, in the dehydrated Cu(I)Y zeolites, Cu$^+$ ions are located inside the small cavities, sodalite cages, or hexagonal prisms.[5]

---

(7) T. A. Egerton and F. S. Stone, *Trans. Faraday Soc.*, **66**, 2364 (1970).

(8) M. C. Sneed, J. L. Maynard, and R. C. Brasted, in "Comprehensive Inorganic Chemistry," Vol. II, Van Nostrand, New York, N. Y., 1954, Chapter 1.

(9) A. T. Larson and C. S. Teitsworth, *J. Amer. Chem. Soc.*, **44**, 2878 (1922).

(10) R. Stewart and D. G. Evans, *Anal. Chem.*, **35**, 1315 (1963).

(11) A. F. Scott, L. L. Wilkening, and B. Rubin, *Inorg. Chem.*, **8**, 2533 (1969).

(12) J. O. Alben, L. Yen, and N. J. Farrier, *J. Amer. Chem. Soc.*, **92**, 4475 (1970).

(13) G. Rucci, C. Zanottera, M. P. Lachi, and M. Camia, *Chem. Commun.*, 652 (1971).

(14) R. Mason and G. Rucci, *Chem. Commun.*, 1132 (1971).

(15) Summarized in "Gmelins Handbuch der anorganischen Chemie. Kupfer," Teil B, Verlag Chemie, GMBH, Weinheim/Bergstrasse, 1958, pp 233–237.

(16) J. H. Little in "Infrared Spectra of Adsorbed Species," Academic Press, New York, N. Y., 1966, p 73.

(17) C. L. Angell and P. C. Schaffer, *J. Phys. Chem.*, **70**, 1413 (1966).

(18) R. D. Cowan, *J. Chem. Phys.*, **18**, 1101 (1950).

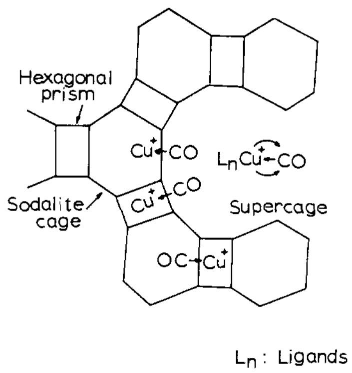

Figure 5. Schematic view of Cu^+–CO complexes in Y zeolite.

Like Cu(II)Y zeolites the cations could be in sites I, I′, or II′, positions where they are not exposedto the supercages. They could be so coordinated to the oxide ions of the zeolite lattice that the π bonding would not be effectively involved in the carbonyl complexes. As a result, the infrared absorption band was observed at 2160 cm^{-1}. The Cu^+–CO interaction in zeolite is schematically shown in Figure 5.

The situation was different when other ligands were present. Because of the complex formation, Cu^+ would be in different locations, most likely in the supercages. It has been shown that when ammonia is adsorbed in Cu(I)Y samples, the Cu^+ ions are pulled out of the small cavities and form cuprous ammines in the supercage.[5] The white sample turns deep blue immediately after the addition of oxygen, which can enter only the supercage at 25°, indicating the formation of cupric ammines as soon as the Cu^+ ions have been oxidized to Cu^{2+} ions, while in the absence of ammonia, no oxidation takes place, as is indicated by esr monitoring of the Cu^{2+} signals. Therefore, the Cu^+–CO complexes in the presence of ammonia must be located in the supercages, as is schematically shown in Figure 5. With the effect of π bonding between Cu^+ and CO, the infrared band of C–O stretching thus shifted to 2080 cm^{-1}, which is 63 cm^{-1} below the gas frequency and 80 cm^{-1} below that observed without preadsorbed ammonia.

The same was also conspicuously observed when ethylenediamine was used as the ligand to form cuprous complexes in the supercages. In addition to a band at 2090 cm^{-1}, it is interesting that another band at 1916 cm^{-1} showed up, which indicated the formation of bridging carbonyls. This is quite similar to the work of Rucci, Zanottera, Lachi, and Camia,[13] in which the compound Cu(en)(CO)Cl had been prepared and an infrared band at 1905 cm^{-1} had been observed. A binuclear complex ($[(en)Cu(CO)_2Cu(en)]Cl_2$) was attributed to the formation of bridging carbonyl groups. In the Cu(I)Y zeolite, there were 21 Cu^+ ions per unit cell, which corresponds to about three Cu^+ ions per supercage. Certainly, there were enough to form bridging CO groups. These groups disappeared after the sample had been evacuated above 200°. According to Rucci, *et al.*, the other complex [Cu(en)CO]Cl, which showed an infrared band at 2080 cm^{-1}, existed in equilibrium with the binuclear complex in methanol solution. The former was predominant at temperatures above −30°.

If pyridine formed complexes with Cu^+ ions in zeolite, a C–O band at 2120 cm^{-1} was observed. It is slightly lower than the gas frequency; however, it is higher than the value of 2069 cm^{-1} reported on cuprous chloride dissolved in pyridine.[12] The local environment of Cu^+–py complexes in zeolite might be somewhat different from that in the solution. The steric hindrance to the complexes by the zeolite lattice could affect the frequency of the terminal carbonyl group. At any rate, the frequency is 40 cm^{-1} lower than that in the absence of ligands.

In addition to forming complexes with Cu^+ ions, ammonia, ethylenediamine, and pyridine can also be adsorbed on other sites of the zeolite lattice, especially on the acidic sites. Ethylenediamine and pyridine are considerably larger than ammonia molecules and they cannot possibly enter the small cavities. The supercages would be filled with ethylenediamine or pyridine when they were adsorbed at 25° and 10 Torr. This could be the reason why no CO absorption bands were observed. However, desorption at 25° or at 100° would remove some of the weakly adsorbed molecules so that carbonyls could be formed. This was not the case for ammonia. Adsorption measurement indicated that at 25° and 10 Torr, the supercages of the Cu(I)Y zeolite were not filled with ammonia.[3] Therefore, carbonyls could be readily formed without desorbing part of the ammonia. Upon successive removal of ligands at higher temperatures, Cu^+ ions would move progressively back into the small cavities. A progressive increase in the C–O stretching frequency with increase in desorption temperature is indicated in Table II.

Table II. Effect of Desorption Temperature of the Ligands on the C–O Stretching Frequency of Carbonyls in Cu(I)Y (75%) Zeolite (with CO at 25° and 40 Torr)

	Desorption temperature, °C				
Ligand	25	120	200	300	400
NH_3	2080, 2125	2135, 2150			2160
en	1916, 2090	1918, 2110	2120	2150	2170
py	2130, 2190(?)	2120	2130	2140	2155

Infrared spectra and colors of copper amine complexes in Y zeolites are similar to those of copper compounds of ammines,[19] ethylenediamine,[20] and pyridine.[21,22] More detailed information on the Cu–N vibration in zeolites is not available because of the lack of transmission below 1200 cm^{-1}. In the spectrum of ammonia-adsorbed Cu(I)Y sample, a band at 1470 cm^{-1} was observed which did not appear in the original Cu(II)Y zeolite. An experiment showed that this band disappeared after the Cu(I)Y sample had been oxidized either by treating with oxygen at 400° for 40 hr or by introducing oxygen at 25° to the ammonia-preadsorbed sample. Apparently, the band at 1470 cm^{-1} was only associated with the reduced sample. If this is attributed to ammonium ions, then Brønsted acid sites could have been formed in the Cu(I)Y zeolite

(19) G. M. Barrow, R. H. Krueger, and F. Basolo, *J. Inorg. Nucl. Chem.*, **2**, 340 (1956).

(20) D. B. Powell and N. Sheppard, *Spectrochim. Acta*, **17**, 68 (1961).

(21) N. S. Gill, R. H. Nuttall, D. E. Scaife, and D. W. A. Sharp, *J. Inorg. Nucl. Chem.*, **18**, 79 (1961).

(22) A. H. Lewin and R. J. Michl, *Chem. Commun.*, 1400 (1971).

during the reduction process. A band at 1450 cm^{-1} was observed on rehydrated silica–alumina and was assigned to the formation of ammonium ions by Eischens and Pliskin.[23] Note that in the present study, the zeolite had always been treated at temperatures below 400°. According to Naccache and Ben Taarit,[24] Lewis acid centers were formed if Cu(II)Y was reduced by carbon monoxide at 500°. They proposed a scheme in which Cu^{2+} ions were reduced to Cu^{+} ions by carbon monoxide. The scheme cannot explain satisfactorily the present observation. At any rate, further investigation would be necessary to understand more about the reduction process.

[23] R. P. Eichens and W. A. Pliskin, *Advan. Catal. Relat. Subj.*, 1 (1958).

[24] C. M. Naccache and Y. Ben Taarit, *J. Catal.*, **22**, 171 (1972).

Complexes as Ligands. Structure and Metal Exchange of β-Diketonate–Schiff's Base Adducts Containing Copper(II) and Cobalt(II)

Nelson B. O'Bryan, Thomas O. Maier, Iain C. Paul, and Russell S. Drago*

Contribution from the W. A. Noyes Laboratory, University of Illinois, Urbana, Illinois 61801. *Received April 2, 1973*

Abstract: In the course of investigating adducts formed by bis(hexafluoroacetylacetonato)copper(II), the reaction of this Lewis acid with the Lewis base, *N,N'*-ethylenebis(salicylideniminato)cobalt(II), was investigated. During the characterization of this structure by mass spectroscopy, magnetic susceptibility, and X-ray crystal structure determination, it was discovered that the metals had interchanged primary coordination spheres. The interchange is rapid in methylene chloride at room temperature. The identical adduct is formed by the addition of *N,N'*-ethylenebis(salicylideniminato)copper(II) to bis(hexafluoroacetylacetonato)cobalt(II). The crystals of $Cu(C_{16}H_{14}N_2O_2)Co(C_5HF_6O_2)_2$ are triclinic with a = 18.412 (5) Å, b = 9.419 (3) Å, c = 12.044 (3) Å, α = 113.90 (2)°, β = 123.25 (2)°, and γ = 89.20 (2)°; the unit cell, space group $P\bar{1}$, contains two molecules. The molecule contains a copper atom with square-planar coordination and an octahedrally coordinated cobalt atom. The two phenolic oxygen atoms function as bridging atoms between the metal centers.

The cobalt(II) complex of *N,N'*-ethylenebis(salicylidenimine), salen, is one of the first cobalt complexes reported to coordinate molecular oxygen.[1] Accordingly, we are interested in the acid–base chemistry of this complex and its 1:1 adducts. During these studies, we encountered interesting binuclear complexes formed by the reaction of Co(salen) and fluorinated β-ketoenolate copper(II) complexes. Reports of salen complexes acting as ligands to form binuclear compounds have appeared in the literature.[2] These binuclear complexes are believed to form because of the ability of the salen phenolic oxygen atoms to function as bridging atoms. However, no confirmatory crystal and molecular structure data have been reported. Because of our interest in Co(salen) and fluorinated β-ketoenolate copper(II), we have investigated the physical properties, structure, and reactivities of these copper–cobalt systems.

Our investigations have shown that reactions between Co(salen) and fluorinated β-ketoenolate copper(II) complexes produce binuclear compounds in which the metals have exchanged coordination spheres. These products are therefore best described as addition compounds of Cu(salen) and fluorinated β-ketoenolate cobalt(II) complexes. For most of the studies reported here, the adduct was prepared directly by the addition of Cu(salen) to bis(hexafluoroacetylacetonato)cobalt(II).

Experimental Section

N,N'-Ethylenebis(salicylideniminato)cobalt(II) [Co(salen)],[3] bis(hexafluoroacetylacetonato)copper(II) [$Cu(hfa)_2$],[4] and diaquobis(hexafluoroacetylacetonato)cobalt(II) [$Co(hfa)_2 \cdot 2H_2O$][5] were prepared by methods described in the literature. *N,N'*-Ethylenebis(salicylideniminato)copper(II) [Cu(salen)] and the nickel analog, Ni(salen), were prepared by substituting copper acetate or nickel acetate for cobalt acetate in the procedure described for Co(salen).[3]

Cu(salen)Co(hfa)$_2$. The adduct was originally prepared using a Soxhlet extractor because of the low solubility of Co(salen) in methylene chloride. Co(salen) (3.0 g, 9.3 mmol) was placed in the extraction thimble; $Cu(hfa)_2$ (4.4 g, 9.3 mmol) was dissolved in 100 ml of methylene chloride. The extraction was allowed to continue until most of the Co(salen) had been removed from the thimble (48 hr). The methylene chloride was pumped off and the residue washed with carbon tetrachloride to remove unreacted $Cu(hfa)_2$. The product was recrystallized from methylene chloride.

The adduct was best prepared, however, by stirring 1 mmol (330 mg) of Cu(salen) and 1 mmol (493 mg) of $Co(hfa)_2 \cdot 2H_2O$ in 100 ml of methylene chloride for 2 hr. Partial evaporation of the solvent and overnight storage in a refrigerator produced small, dark red crystals. The product was recrystallized from methylene chloride. *Anal.* Calcd: C, 38.89; H, 2.01; Co, 7.34; Cu, 7.91. Found: C, 39.15; H, 2.06; Co, 7.39; Cu, 7.67.

Ni(salen)Co(hfa)$_2$. This orange-red complex can be prepared using the procedure described for Cu(salen)Co(hfa)$_2$. *Anal.* Calcd: C, 39.13; H, 2.02; Co, 7.38; Ni, 7.31. Found: C, 39.09; H, 1.81; Co, 7.52; Ni, 7.15.

Magnetic Susceptibility. Solution susceptibilities were measured with a JELCO 60-MHz nmr using the Evans method.[6] Temperature-dependent studies on the solid complex were done with a PAR

---

[1] T. Tsumaki, *Bull. Chem. Soc. Jap.*, 13, 252 (1938).

[2] S. J. Gruber, C. M. Harris, and E. Sinn, *J. Inorg. Nucl. Chem.*, **30**, 1805 (1968), and references therein.

[3] R. H. Bailes and M. Calvin, *J. Amer. Chem. Soc.*, **69**, 1880 (1947).

[4] W. R. Walker and N. C. Li, *J. Inorg. Nucl. Chem.*, 27, 2255 (1965).

[5] F. A. Cotton and R. H. Holm, *J. Amer. Chem. Soc.*, **82**, 2979 (1960).

[6] D. F. Evans, *J. Chem. Soc.*, 2003 (1959).