

Table I. Spin Concentration of  $\text{Cu}_{18}\text{Na-Y}$  upon Addition of Pyridine at 100 °C

py molecules ads/ $\text{Cu}^{2+}$	spin concn $\times$ $10^{-20}$ , spins/g of ZY <sup>b</sup>	mol of $\text{Cu}^{2+}$ / g of ZY <sup>b</sup> $\times 10^4$
0	6.2	1.0 (1.4) <sup>a</sup>
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

<sup>a</sup> Obtained from chemical analysis. <sup>b</sup> ZY = zeolite Y.

Table I shows that the total  $\text{Cu}^{2+}$  concentration remained constant upon the stepwise addition of pyridine, under the conditions described previously, and, furthermore, within experimental error the  $\text{Cu(II)}$  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  $\text{Cu}^+$ . Furthermore, together with the EPR data they confirm that all of the  $\text{Cu}^{2+}$  ions participated in complex formation when a stoichiometric amount of pyridine was present.

Additional evidence for the formation of the  $[\text{Cu}^{\text{II}}(\text{py})_4]^{2+}$  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  $\text{Cu}_{18}\text{Na-Y}$  after dehydration at 400 °C had a band maximum at 10800  $\text{cm}^{-1}$  and a shoulder around 14300  $\text{cm}^{-1}$ . Adsorption of pyridine at 100 °C resulted in the disappearance of these bands and the formation of an intense new band at 17300  $\text{cm}^{-1}$ . This spectrum is in excellent agreement with the single-crystal spectrum of  $[\text{Cu}/\text{Cd}(\text{C}_5\text{H}_5\text{N})_4]\text{S}_2\text{O}_8$ , for which a band at 17200  $\text{cm}^{-1}$  was assigned to the  ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$  and  ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$  transitions.<sup>10</sup>

Clearly the results described here confirm the earlier assignment of the  $\text{Cu}^{\text{II}}\text{-py}$  complex as  $[\text{Cu}^{\text{II}}(\text{py})_4]^{2+}$ . 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  $\text{Cu}^{\text{II}}\text{-ethylenediamine}$  case for which mono, bis, and tris complexes were observed.<sup>11</sup> 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  $\text{Cu}^{2+}$  ion in the complex, which may be far removed from the oxide ions of the lattice, has been addressed by Gallezot et al.<sup>12</sup> 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<sup>13</sup> 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  $[\text{Cu}^{\text{II}}(\text{py})_4]^{2+}$  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,<sup>14</sup>

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

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**Registry No.**  $[\text{Cu}^{\text{II}}(\text{py})_4]^{2+}$ , 19724-33-5.

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### X-ray Photoelectron Spectra of Copper(III) Complexes

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We have recently reported the X-ray photoelectron spectrum of a number of metal-biureto complexes, one of which was a copper(III) system.<sup>1</sup> The spectrum of this species, potassium bis(biureto)cuprate(III),  $\text{KCu}(\text{bi})_2$ , 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.<sup>2</sup> To our knowledge these are the only two reports of XPS for copper(III).<sup>3</sup> 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<sup>4,5</sup>), 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.<sup>6</sup> 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.<sup>7</sup> We have prepared salts with either potassium or tetra-*n*-butylammonium cations. Figure

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Table I. Copper XPS Parameters

compd	Cu 2p <sub>3/2</sub> binding energies, eV		Cu 2p <sub>1/2</sub> binding energies, eV		I <sub>satellite</sub> /I <sub>total</sub> <sup>a</sup>	Line width of Cu 2p <sub>3/2</sub> main peak, eV
	main	satellite	main	satellite		
Cu(o-phen(bi) <sub>2</sub> ) <sub>2</sub> <sup>2-</sup>	933.7	942.8	953.8	962.0	0.30	2.5
Cu(o-phen(bi) <sub>2</sub> ) <sub>2</sub> <sup>-</sup>	934.4	943.6	954.8	963.1	0.29	3.3
Cu(en(bi) <sub>2</sub> ) <sub>2</sub> <sup>2-</sup>	933.8	942.8	953.6	962.5	0.28	2.9
Cu(en(bi) <sub>2</sub> ) <sub>2</sub> <sup>-</sup>	934.6	943.3	954.3	963.0	0.30	4.2
Cu(bi) <sub>2</sub> <sup>2-</sup>	933.7	942.4	953.8	962.2	0.30	3.0
Cu(bi) <sub>2</sub> <sup>-</sup>	934.7	942.4	954.8	962.1	0.25	4.2

<sup>a</sup> For Cu 2p<sub>3/2</sub> region.

1 shows the Cu 2p<sub>3/2</sub> spectra for (a) Cu(o-phen(bi)<sub>2</sub>)<sub>2</sub><sup>2-</sup>, (b) Cu(o-phen(bi)<sub>2</sub>)<sub>2</sub><sup>-</sup> (c) Cu(en(bi)<sub>2</sub>)<sub>2</sub><sup>2-</sup>, and (d) Cu(en(bi)<sub>2</sub>)<sub>2</sub><sup>-</sup>.<sup>8</sup> The copper spectra are virtually identical for both the potassium and tetra-*n*-butylammonium salts. It is immediately apparent that these copper(III) species, just as Cu(bi)<sub>2</sub><sup>-</sup> reported earlier,<sup>1</sup> show well-defined satellites. Table I summarizes the X-ray photoelectron spectra parameters for the copper(II) and copper(III) complexes studied as well as those for the bis(biureto)cuprates previously reported.

The most important observation from these data is the presence of rather intense satellites in the 2p spectra, consistent with our earlier observations for Cu(bi)<sub>2</sub><sup>-</sup>. As we have discussed previously,<sup>1</sup> the origin of the satellites cannot be due to X-ray induced reduction of the copper(III) to copper(II) during the measurement. These spectra were recorded at ca. 100 K which, with our instrument, has proven sufficient to prevent the photodecomposition sometimes occurring at ambient temperatures.<sup>9</sup> In addition, the spectral properties are sufficiently different that the spectra could not arise from the same species.

Inspection of the main peak binding energies reveals that the copper(III) complexes always show a higher binding energy than the corresponding copper(II) system, as one would expect. However, the differences between the copper(III) and copper(II) main peak binding energies, for a given ligand system, are not very large (≤1 eV). On the basis of a reported empirical correlation of copper 2p binding energies with the charge on copper in a series of copper compounds,<sup>10</sup> one can estimate that the copper(III) has only 0.2–0.3 higher real charge than the copper(II). This is a clear experimental indication of the fundamental reason for the stability of such copper(III) systems. The strong electron-donating ability of the deprotonated nitrogen donor atoms provides a low actual charge on the copper, even in the formal copper(III) oxidation state. The absolute magnitudes of the copper(III) binding

energies are, in fact, lower than those found for a number of copper(II) compounds (CuF<sub>2</sub>, 938.5 eV; CuO, 935.7 eV; Cu(oxalate), 935.4 eV; CuCl<sub>2</sub>, 935.1 eV).<sup>11,12</sup> The rather small change in main peak binding energy (~1 eV) and resulting small change in formal charge on copper (~0.3 electron) as an electron is removed from one of the copper(II) species indicates that a significant amount of the electron density removed comes, in fact, from the ligand system.

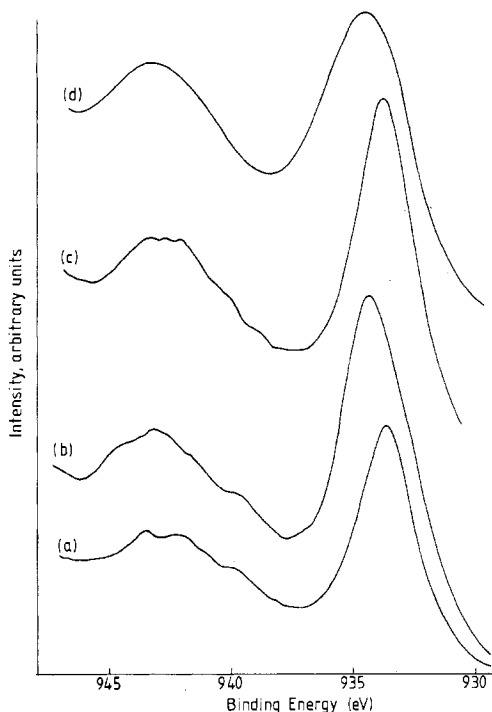
The satellite structure in the complexes is rather similar for the two oxidation states. The binding energy difference between the main and satellite peaks is always on the order of 7–9 eV. While, for some Cu(III)–Cu(II) pairs, this separation will vary by as much as 1 eV, for others it is nearly the same. Likewise, the satellite intensity in the 2p<sub>3/2</sub> region accounts for approximately 30% of the total intensity, regardless of oxidation state. A consistent difference in the spectral parameters for the two oxidation states is the line width (full width at half maximum intensity) of the main peak. The copper(III) spectra always demonstrate a broader main peak than do those for copper(II), although the main copper(III) peaks are always symmetrical.

Earlier literature attributed satellite structure in transition-metal compounds to the presence of unpaired electrons. This was undoubtedly a conclusion based on empirical observations. Subsequent workers have pointed out explicitly that paramagnetism is not a cause of satellite structure.<sup>6b,13</sup> Nevertheless, the empirical observations for the first-row transition metals have, in general, shown stronger satellite structure in paramagnetic systems than in diamagnetic compounds. The data presented here, however, demonstrate clearly that intense satellites can indeed be observed in diamagnetic transition-metal complexes. If one adopts the charge-transfer formalism for the origin of the satellites in copper(II),<sup>6c,d</sup> there is no apparent reason to expect an absence of satellites in copper(III). The similar intensities observed for the satellites in the copper(II)–copper(III) pairs (Table I) are probably fortuitous. Larsson's treatment of satellite structure in copper(II), as well as supporting molecular orbital or Xα calculations,<sup>6c,d</sup> would lead one to the conclusion that the satellite intensity per available orbital for copper(III) should be somewhat lower than for copper(II). However, two b<sub>1g</sub>–b<sub>1g</sub>\* spin orbitals are available for charge transfer in copper(III), which lead to the same shake-up state, rather than the one available in copper(II). This degeneracy would double the expected intensity per available orbital for copper(III). Apparently the two opposing factors are of approximately equal magnitude resulting in similar observed satellite intensities for copper(II) and copper(III).

In our view the presence of satellites in these copper(III) systems appears to be consistent with theoretical discussions of satellite structure for copper. However, the nickel(II)

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**Figure 1.** Copper  $2p_{3/2}$  spectra for (a)  $\text{Cu}(o\text{-phen}(\text{bi})_2)_2^-$ , (b)  $\text{Cu}(o\text{-phen}(\text{bi})_2)^-$ , (c)  $\text{Cu}(\text{en}(\text{bi})_2)_2^-$ , and (d)  $\text{Cu}(o\text{-en}(\text{bi})_2)^-$ .

analogue  $\text{K}_2\text{Ni}(\text{bi})_2$  is isoelectronic with  $\text{KCu}(\text{bi})_2$  yet shows no satellite structure nor do other low-spin nickel(II) systems.<sup>1</sup> The qualitative theoretical arguments employed to explain the presence of satellites in copper appear to be valid for nickel(II) in  $\text{K}_2\text{Ni}(\text{bi})_2$ . It is hoped that this inconsistent behavior for isoelectronic nickel(II) and copper(III) will be successfully addressed by theoreticians thus improving the current model for satellite structure in transition-metal XPS.

### Experimental Section

The complexes were prepared following procedures reported in the literature.<sup>7</sup> Both potassium and tetra-*n*-butylammonium salts of the complexes were investigated. The ligands were prepared by the method of Birker et al.<sup>7a,14</sup> Chemicals were reagent grade. *o*-Phenylene-diamine was recrystallized immediately before use.

XPS measurements were carried out on a Varian V-IEE 15 high-resolution electron spectrometer equipped with a 620 on-line computer (8K). During the course of the measurements the sample was maintained at about 100 K by cooling with liquid nitrogen. The samples were run as finely ground powders dusted onto the backing of a one-sided adhesive Cellotape (Scotch Tape, 3M Co.) which was attached to the cylindrical sample holder. The spectra were standardized with the  $\text{C}_{1s}$  aliphatic hydrocarbon line for which a binding energy of 284.0 eV was assigned.<sup>15</sup>

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**Registry No.**  $\text{Cu}(o\text{-phen}(\text{bi})_2)_2^-$ , 71964-24-4;  $\text{Cu}(o\text{-phen}(\text{bi})_2)^-$ , 71964-25-5;  $\text{Cu}(\text{en}(\text{bi})_2)_2^-$ , 71964-26-6;  $\text{Cu}(\text{en}(\text{bi})_2)^-$ , 71964-27-7;  $\text{Cu}(\text{bi})_2^{2-}$ , 57674-47-2;  $\text{Cu}(\text{bi})_2^-$ , 71964-28-8.

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## Chemistry of Trifluoromethyl Compounds. 2. Synthesis and Characterization of Bis(pyridine)bis(trifluoromethyl)zinc

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There has been interest in the use of bis(trifluoromethyl)mercury as a source for trifluoromethyl groups by ligand-exchange reactions.<sup>1</sup> Exchange reactions involving  $\text{Hg}(\text{CF}_3)_2$  have concentrated on the main-group elements, although a report has appeared on the dimethylcadmium/bis(trifluoromethyl)mercury system.<sup>2</sup>

In a previous paper,<sup>3</sup> we reported  $^{19}\text{F}$  NMR evidence for bis(trifluoromethyl)zinc. It was found that facile methyl and trifluoromethyl exchange occurred between dimethylzinc and bis(trifluoromethyl)mercury in pyridine. We report here the isolation of bis(pyridine)bis(trifluoromethyl)zinc from the reaction of dimethylzinc and bis(trifluoromethyl)mercury in pyridine. Chemical and physical properties of this compound are presented. The stability of the resulting bis(trifluoromethyl)zinc compound is due to the pyridine, which as a result of its electron-withdrawing trifluoromethyl groups evidently satisfies the electronic properties of zinc.

### Experimental Section

**Preparation of  $\text{Zn}(\text{CF}_3)_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ .**  $\text{Hg}(\text{CF}_3)_2$  (0.521 g, 1.54 mmol) was dissolved in 4.0 mL of dried pyridine. To this was added 0.071 g (0.74 mmol) of  $\text{Zn}(\text{CH}_3)_2$ . The solution was stirred for approximately 8 h at room temperature. During this time, the initially clear solution turned red-brown. The volatile materials were removed under vacuum over a 2-day period in order to remove all unreacted  $\text{Hg}(\text{CF}_3)_2$ . The volatile materials were identified as pyridine,  $\text{Hg}(\text{CF}_3)(\text{CH}_3)$ , and  $\text{Hg}(\text{CF}_3)_2$ . The light brown residue remaining was identified as bis(trifluoromethyl)zinc by its  $^{19}\text{F}$  NMR spectrum in pyridine solution.<sup>3</sup> No other trifluoromethyl-containing compounds were identified from both  $^{19}\text{F}$  and  $^1\text{H}$  NMR spectra. The purity of the compound was determined by mass spectral analysis. No mercury-containing compounds were found to be present. The sample was stored in evacuated containers and all subsequent transfers were made in an oxygen-free argon drybox to exclude exposure to moisture. Recrystallization was accomplished by dissolving the light brown residue in benzene. Filtration by Schlenk-type apparatus removed insoluble polymeric materials. Removal of the benzene by vacuum distillation resulted in a light brown residue of  $\text{Zn}(\text{CF}_3)_2 \cdot 2\text{py}$ . Purification by this method resulted in 0.22 g (82% yield) of material.

Anal. Calcd for  $\text{ZnC}_{12}\text{H}_{10}\text{F}_6\text{N}_2$ : C, 39.86; H, 2.79; F, 31.53; N, 7.75; Zn, 18.08. Found: C, 40.20; H, 3.02; F, 29.92; N, 7.68; Zn, 16.87.

**Infrared Spectrum.** The infrared spectrum of  $\text{Zn}(\text{CF}_3)_2 \cdot 2\text{py}$  in a KBr disk was recorded on a Perkin-Elmer 180 infrared grating spectrophotometer: 3120 (vw), 3080 (vw), 3060 (vw), 2920 (vw), 2885 (vw), 2820 (vw), 1650 (w), 1606 (s), 1572 (w), 1490 (m), 1449 (s), 1257 (w), 1220 (m), 1161 (sh), 1144 (s), 1130 (s), 1070 (m), 1042 (m), 1015 (m), 960 (s), 945 (s), 880 (w), 756 (s), 700 (s), 680 (w), 635 (m), 500 (w), 421 (w), 416 (w), 288 (w), 245 (w)  $\text{cm}^{-1}$ . (See Figure 1.)

**Nuclear Magnetic Resonance Spectra.**  $^{19}\text{F}$  and  $^1\text{H}$  NMR spectra were recorded on a Varian EM-390 NMR spectrometer operating at 84.56 and 90 MHz, respectively. Interfaced with the instrument was a Nicolet NMR-80 system employing a Bruker Correlation Program for signal averaging. Proton-decoupled  $^{13}\text{C}$  NMR spectra were recorded on a Varian XL-100 NMR spectrometer operating at 25.2 MHz interfaced with a Nova 1210 computer for Fourier

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