Notes

Contribution from the Department of Chemistry, Faculty of Science and Technology, Kinki University, Kowakae, Higashi-Osaka, 577 Japan

New Mixed-Ligand Copper(I) Complexes with 2,2′-Bipyridine and Their NMR Spectra

Susumu Kitagawa,* Megumu Munakata, and Noboru Miyaji

Received October 15, 1981

Recent interest in copper proteins has centered on the design, preparation, and characterization of small-molecule complexes[1] of copper(I), which offer insight into the coordination chemistry of copper(I) in metalloproteins. The paucity of literature on Cu(I) ternary complexes that are of biological significance is mainly due to the lack of physicochemical methods to characterize Cu(I) complexes in solution. ^{1}H and ^{13}C NMR spectra can provide well-resolved signals that yield useful information about Cu(I) complexes in solution because of their diamagnetism. Furthermore, several species existing in solution are simultaneously detected by NMR spectroscopy. We now present new ternary Cu(I) complexes and their ^{1}H and ^{13}C NMR spectra. The observed chemical shifts are examined in relation to the metal–ligand binding.

Experimental Section

$[Cu(CH_3CN)_4]ClO_4$ was prepared in the usual way.[2] 2,2′-Bipyridine (bpy), $P(C_4H_9)_3$, $P(OCH_3)_3$, $P(OC_4H_9)_3$, and $P(OC_6H_5)_3$ were commercially available, and they were recrystallized or distilled before use. $C_6H_{11}NC$ was synthesized according to the literature.[3]

The mixed-ligand Cu(I) complexes were prepared under an argon atmosphere by simultaneously adding both bpy (5 mM) and L (10 mM) to a 5 mM acetone-d_6 solution of $[Cu(CH_3CN)_4]ClO_4$. This solution was transferred into an NMR sample tube and sealed therein. $[Cu(bpy)(CO)_2]ClO_4$ was prepared under CO atmosphere.

^{1}H and ^{13}C NMR spectra were recorded on a JEOL FX 200 FT NMR spectrometer, operating at 199.5 (^{1}H) and 50.10 (^{13}C) MHz. For ^{1}H NMR measurements, 128 transients were accumulated with the use of 13-μs pulses (90°), and 4K data points were collected over a bandwidth of 1250 Hz. For ^{13}C NMR measurements, 10000–12000 transients were accumulated with the use of 5-μs pulses (45°), and 8K data points were collected over a bandwidth of 12000 Hz. The temperature was set at 24 (^{1}H) and 31 °C (^{13}C). $(CH_3)_4Si$ was used as the internal standard for both ^{1}H and ^{13}C NMR spectra.

Results and Discussion

The ternary complexes $[Cu(bpy)L_2]ClO_4$ (L = $P(C_4H_9)_3$, $P(OCH_3)_3$, $P(OC_4H_9)_3$, $P(OC_6H_5)_3$, and $C_6H_{11}NC$) quantitatively formed when equimolar quantities of bpy and L were added to the solution of $[Cu(CH_3CN)]_4ClO_4$. $[Cu(bpy)(CO)_2]ClO_4$ also formed at 25 °C when CO gas was passed through the solution. This formation is well illustrated by both ^{1}H and ^{13}C NMR spectra. The obtained spectra are dissimilar from those of $[Cu(bpy)_2]ClO_4$[4] and metal-free bpy. As shown in Figure 1, the ^{1}H NMR spectra or $[Cu(bpy)L_2]ClO_4$ show four well-resolved resonance peaks of coordinated bpy with equal intensities in the aromatic region, while their ^{13}C NMR spectra give five resonance signals of coordinated bpy in the region 120–160 ppm. The observed ^{1}H and ^{13}C chemical shifts are listed in Table I.

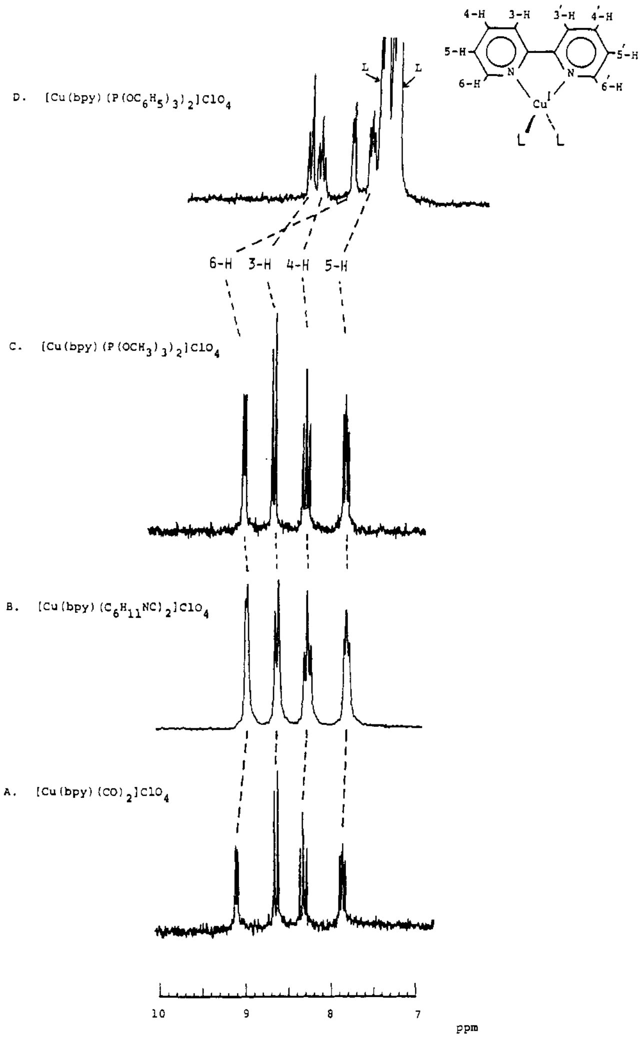

Figure 1. 200-MHz ^{1}H NMR spectra at 25 °C in the downfield region of a $(CD_3)_2CO$ solution 5 mM in total Cu(I) ion: (A) spectrum of $[Cu(bpy)(CO)_2]ClO_4$, which formed alone when CO gas was passed through the solution containing $[Cu(CH_3CN)_4]ClO_4$ and bpy (molar ratio 1:1); (B–D) spectra obtained from the solution containing $[Cu(CH_3CN)_4]ClO_4$, bpy, and L (molar ratio 1:1:2). The observed shift is referenced against internal Me_4Si. L denotes the signals of coordinated $P(OC_6H_5)_3$.

The methyl protons of coordinated CH_3CN in $[Cu(CH_3CN)_4]ClO_4$ resonate at 2.17 ppm, while those of metal-free CH_3CN shifted upfield (2.05 ppm). All the ^{1}H NMR spectra of solutions containing ternary complexes show a methyl signal at 2.05–2.06 ppm of metal-free CH_3CN and no signals of metal-free bpy, which indicates the complete formation of $[Cu(bpy)L_2]ClO_4$. The position of these methyl signals[5] is a good indicator of the coordination of the second ligand L.

bpy having π-electronic structure is involved in π back-bonding with the Cu(I) ion in $[Cu(bpy)_2]ClO_4$, which shows an intense metal-to-ligand charge transfer (MLCT) band at

---

(1) Kitagawa, S.; Munakata, M. *Inorg. Chem.* **1981**, *20*, 2261.

(2) Andrieth, L. F.; Bailar, J. C.; Fernelius, W. C.; Johnson, W. C.; Kirk, R. E. *Inorg. Synth.* **1946**, *2*, 1.

(3) Ugi, I.; Meyr, R. *Chem. Ber.* **1960**, *93*, 239.

(4) $[Cu(bpy)_2]ClO_4$ encounters a chemical exchange effect at 25 °C, and all the signals are averaged to become a broad line. When the solution is cooled at -90 °C, well-resolved signals are obtained: 8.90, 7.88, 8.41, and 8.90 ppm for 6-, 5-, 4-, and 3-protons, respectively.

(5) The ^{13}C chemical shifts, δ_{CH_3}, of coordinated and metal-free CH_3CN are 1.29 and 1.40 ppm, respectively. A solution of $[Cu(bpy)L_2]ClO_4$ also gives only a metal-free CH_3 signal.

0020-1669/82/1321-3842$01.25/0

Table I. Observed ^1H and ^{13}C NMR Shifts[a] of $[Cu(bpy)L_2]ClO_4$ in Acetone-d_6

L	H-6	H-5	H-4	H-3	C-2	C-3	C-4	C-5	C-6
bpy[b]	8.67	7.41	7.92	8.48	156.92	124.62	137.59	121.35	149.96
CO	9.13	7.89	8.35	8.67	152.65	127.89	141.47	123.31	151.66
$C_6H_{11}NC$	8.98	7.81	8.27	8.63	*c*	127.04	139.72	122.99	150.64
$P(C_4H_9)_3$	8.99	7.82	8.27	8.68	153.00	127.25	140.13	123.51	150.93
$P(OCH_3)_3$	9.06	7.86	8.33	8.70	152.92	127.63	140.71	123.51	151.31
$P(OC_4H_9)_3$	9.12	7.87	8.33	8.73	153.24	127.89	140.91	123.98	151.48
$P(OC_6H_5)_3$	7.65	7.43	8.02	8.16	157.53	126.99	139.95	123.40	150.42

[a] Shifts in ppm from Me_4Si at 25 (^1H) and 31 °C (^{13}C). Error limit ±0.01 (^1H) and ±0.03 ppm (^{13}C). [b] Signals of a metal-free bpy. [c] Signals of the C-2 nucleus were hardly detected due to low S/N ratio.

440 nm.[1] In ternary complexes, the absorption spectra of $[Cu(bpy)L_2]$, however, reveal a blue shift (<360 nm) of the MLCT band, exhibiting a strong contribution of L to π back-bonding of Cu(I) and bpy. This shows that the good π acceptor effectively suppresses the π back-bonding[6] between Cu(I) and bpy as a consequence of competing with bpy. NMR spectra also provide valuable information about metal–ligand binding in addition to the structure in solution. C-4 of bpy is located at the position para to a pyridine nitrogen. The shift of C-4 is available because it is attributable to the variation of the charge based on a through-bond interaction. Among the ternary complexes in Table I, the order in upfield shift of the C-4 resonance signal is $CO < P(OC_4H_9)_3 < P(OCH_3)_3 < P(C_4H_9)_3 < C_6H_{11}NC$. It is to be noted in Table I that the above order is in fairly good agreement with that obtained from the shift of H-4: the increase in shielding of C-4 just accompanies the increase in shielding of H-4. Good correlation between ^1H and ^{13}C chemical shifts has been also found in transition-metal cyclopentadienyl derivatives.[7] Cyclopentadienyl carbon resonance is more shielded as the shielding of the corresponding proton shift increases. The obtained order expressed with ligand L is regarded as the reverse order of π-acceptor capability of L in complexes $[Cu(bpy)L_2]ClO_4$: $CO > P(OC_4H_9)_3 > P(OCH_3)_3 > P(C_4H_9)_3 > C_6H_{11}NC$. This order agrees with that obtained from carbonyl stretching frequencies of the mixed-ligand Co and Mo complexes containing CO,[8] indicating that phosphines, phosphites, isocyanides, and CO act as good π acceptors and exert a trans-influence-like effect on another ligand in the mixed-ligand transition-metal complexes.

With the use of $M^{II}(phen)_3$ (M^{II} = Ru, Fe, Zn),[9] it has been demonstrated that the metal ion having strong π-back-bonding capability causes an upfield shift of the proton signals of phen. Analogously, the upfield shift of bpy protons of $[Cu(bpy)L_2]ClO_4$ is explained by increased π back-bonding in Cu–bpy and concurrently decreased π back-bonding in Cu–L. In this sense, the π back-bonding of Cu–bpy is controlled by the Cu–L bonding, which is well reflected by the ^1H and ^{13}C resonance shifts.

The C-6 and H-6 shifts are also associated with the variation of the charge in a through-bond interaction, giving an order similar to that obtained for C-4 and H-4. Shifts of C-2 and C-5, however, show a different trend. C-5 is para to the 2,2′-bond of bpy. C-2 and C-5 are affected by the variation of the 2,2′-bond[11] upon coordination.

Finally, we refer to the ^1H chemical shift of $[Cu(bpy)(P(OC_6H_5)_3)_2]ClO_4$. The signal of H-6 shifts upfield (7.65 ppm), while that of the other ternary complexes in Table I falls within the range 8.98–9.13 ppm. H-6 of $[Fe^{II}(bpy)_3]Cl_2$ shows a considerable upfield shift[10] (~1 ppm), which is caused by the magnetic anisotropy of an aromatic ring of a neighboring ligand due to octahedral geometry (through-space interaction), and the signal of H-6 appears near that of H-5. In the case of $[Cu(bpy)_2]ClO_4$,[4] the upfield shift of H-6, whose degree is much smaller than that in $[Fe(bpy)_3]Cl_2$, is also associated with the similar magnetic anisotropy of a neighboring ligand even in tetrahedral geometry. On this basis, H-6 of $[Cu(bpy)L_2]ClO_4$ may also undergo a through-space interaction with a neighboring ligand L having aromatic groups. The anomalous upfield shift of H-6 of $[Cu(bpy)(P(OC_6H_5)_3)_2]ClO_4$ exhibits that the phenyl group of the coordinated $P(OC_6H_5)_3$ is located in the vicinity of the coordinated bpy, and hence, it can exert a magnetic anisotropy effect upon bpy protons. The other protons of bpy may similarly undergo this effect of coordinated $P(OC_6H_5)_3$. Except for the case of $P(OC_6H_5)_3$, the appearance of the H-6 signal near the H-3 signal is characteristic of the ternary Cu(I) complexes in acetone.

In conclusion, the new ternary Cu(I) complexes were selectively prepared in solution by monitoring their ^1H and ^{13}C NMR spectra. The second ligand L delicately controls the π back-bonding between Cu(I) and bpy, whose features are readily revealed by the ^1H and ^{13}C NMR signals of H-4 and C-4, respectively. These findings regarding the shifts serve as a very useful guide for the investigation of mixed-ligand Cu(I) complexes in solution.

Acknowledgment. This work is supported in part by grants from the Ministry of Education of Japan.

Registry No. $[Cu(bpy)(P(C_4H_9)_3)_2]ClO_4$, 82661-29-8; $[Cu(bpy)(P(OCH_3)_3)_2]ClO_4$, 82661-31-2; $[Cu(bpy)(P(OC_4H_9)_3)_2]ClO_4$, 82665-09-6; $[Cu(bpy)(P(OC_6H_5)_3)_2]ClO_4$, 82661-33-4; $[Cu(bpy)(CNC_6H_{11})_2]ClO_4$, 82661-35-6; $[Cu(bpy)(CO)_2]ClO_4$, 82661-37-8; $[Cu(CH_3CN)_4]ClO_4$, 14057-91-1; ^{13}C, 14762-74-4.

---

(6) Kitagawa, S.; Munakata, M.; Higashie, H. *Inorg. Chim. Acta* **1982**, *59*, 219.
(7) Lauterbur, P. C.; King, R. B. *J. Am. Chem. Soc.* **1965**, *87*, 3266.
(8) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 2nd ed.; Wiley: New York, 1972; Chapter 27.
(9) Miller, J. D.; Prince, R. H. *J. Chem. Soc.* **1965**, 3185.
(10) Castellano, S.; Günther, H.; Ebersole, S. *J. Phys. Chem.* **1965**, *69*, 4166.
(11) Williams, R. J. P. *J. Chem. Soc.* **1955**, 137.

Contribution from the Istituto di Chimica Generale and Istituto
di Chimica Analitica dell'Università, 07100 Sassari, Italy, and
from the Istituto di Chimica Generale, CNR Center,
20133 Milano, Italy

ESR Investigation of the Adduct between [1,2-Bis(diphenylphosphino)ethane]bis(3,5-dimethylpyrazolato-*N*)platinum(II) and Copper(II) Sulfate: Evidence of Magnetic Exchange Interaction between Copper(II) Ions Bridged by Sulfato Groups

Franco Cariati,[1a] Giovanni Micera,[1a] Andrea Scozzafava,[1a] Giovanni Minghetti,*[1a] and Guido Banditelli[1b]

Received December 4, 1981

The reaction of the complexes $(L–L)M(pz)_2$ ((L–L) = $(Ph_2PCH_2)_2$, M = Pt; (L–L) = 2,2′-bipyridyl, M = Pt, Pd;

---

* To whom correspondence should be addressed at the Istituto Policattedra di Chimica Analitica e Spettroscopia dell'Università, 07100 Sassari, Italy.