Bicobaltocene$^+$ 1

Bisfulvalene dicobalt$^+$ 3

Biferrocene$^+$ 2

Bisfulvalene diiron$^+$ 4

Figure 1.

ed-valence compounds. Thus, both the $(Cp_2Co)_2^+$ and the $(BFD\text{-}Co)^+$ sytems display substantially larger α values and narrower bandwidths than the diiron analogues. While the observation that $\Delta\bar{\nu}_{1/2} > \Delta\bar{\nu}_{1/2}$(calcd) for $(Cp_2Fe)_2^+$ is consistent with class II behavior,[6b] the opposite finding for $(Cp_2Co)_2^+$ (Table II) suggests that there is sufficient electronic coupling with the latter system to place it at least on the class II/III borderline. The relatively small solvent dependence of $\bar{\nu}_{max}$ observed for $(Cp_2Co)_2^+$ is also indicative of stronger donor–acceptor coupling than can be accomodated strictly in terms of class II behavior.[2]

In particular, since both $(BFD\text{-}Co)^+$ and $(BFD\text{-}Fe)^+$ also display essentially solvent-independent band energies,[4a,b,11] comparison of α values for such extensively delocalized systems[4d] can be misleading given that (2) is obtained from the Hush model.[2,6] Nevertheless, discussion of the overall trends in this and related quantities is likely to remain qualitatively valid.[12] The markedly larger α value, as well as the narrower bandwidth, observed for $(BFD\text{-}Co)^+$ versus $(BFD\text{-}Fe)^+$ (Table II) indicates that the additional metal–metal coupling provided by cobalt also applies to this strong-overlap, doubly linked, structure (Figure 1).

It is also interesting to compare the intervalence band parameters for $(Cp_2Co)_2^+$ and $(BFD\text{-}Fe)^+$. In spite of the additional electronic coupling engendered by the doubly linked ring structure of the latter, the former system nonetheless appears to involve a greater extent of electron delocalization as signaled by a substantially larger α value (Table II). These variations in the extent of electronic coupling brought about by metal substitution, as gauged by differences in α, are at least as large as those engendered by significant or even substantial alterations in the structure of the ring linkages.[3-5]

Estimates of the contribution of electronic delocalization, $\Delta G_{del}°$, to $\Delta G_c°$ can also be readily made, at least for class II systems, from[8]

$$-\Delta G_{del}° = \alpha^2\bar{\nu}_{max} \qquad (4)$$

This yields $\Delta G_{del}°$ values of −0.55 and −0.2 kcal mol^{-1} for $(Cp_2Co)_2^+$ and $(Cp_2Fe)_2^+$, respectively, in acetonitrile. An additional electrostatic contribution to $\Delta G_c°$, $\Delta G_e°$, can be estimated approximately to be −1.0 kcal mol^{-1} under these conditions (acetonitrile, ionic strength 0.1 M).[15] The substantial remaining components of the overall $\Delta G_c°$ values, ca. −3.5 and −2 kcal mol^{-1} for $(Cp_2Co)_2^+$ and $(Cp_2Fe)_2^+$, respectively, are presumably due to further stabilization of the mixed-valence species by inductive effects via the bridging ligand (cf. (bipyridyl)diruthenium systems[8]).

These findings are therefore qualitatively consistent with the aforementioned interpretation of the larger rate constants for $Cp_2Co^{+/0}$ versus $Cp_2Fe^{+/0}$ self exchange in terms of electronic coupling effects. More quantitative comparisons between the bimolecular kinetic and intervalence optical systems, however, are precluded since the latter undoubtedly feature much stronger electronic interactions as a result of a direct linkage between the redox sites. Thus from the usual expression[2,6] $H_{AB} = \alpha\bar{\nu}_{max}$, the electronic matrix coupling element H_{AB} is estimated to be roughly 3.2 and 1.7 kcal mol^{-1} for $(Cp_2Co)_2^+$ and $(Cp_2Fe)_2^+$, respectively.[18] Much smaller H_{ab} values, leading to weakly adiabatic or nonadiabatic electron transfer, are expected for thermally activated outer-sphere processes.[19] Nevertheless, the present results do point clearly to the importance of the orbital symmetry in electron transfer via its influence on the extent of electronic coupling.

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Registry No. **1**, 114031-48-0; **2**, 51263-10-6; **3**, 69365-58-8; **4**, 51140-52-4; **4**·PF_6, 52732-79-3; Cp_2Co, 1277-43-6.

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(12) Strictly speaking, the Hush model and hence eq 2 are only valid for weak coupling between the redox sites. Application of a more sophisticated vibronic coupling model, specifically the PKS treatment,[13] indicates that the Hush theory may significantly underestimate the extent of valence delocalization, even for $(Cp_2Fe)_2^+$.[3e] On the other hand, the PKS treatment itself may not provide an entirely satisfactory description of systems on the class II/III borderline.[14] However, despite these complications, the Hush model remains adequate for the largely qualitative purposes of the present study.

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(15) This estimate is obtained by using the expression $-\Delta G_e° = e^2/D_s d(1 + \kappa d)$, where e is the electronic charge, κ is the reciprocal Debye length, and d is the distance between the metal centers in the mixed-valence compound (see footnote e to Table II). This relation is the Debye-Hückel expression[16] for the work required to form a bimetallocene dication from two unipositive metallocene fragments. It represents the sole contribution to $\Delta G_e°$ since the corresponding electrostatic work for forming the neutral and monocation (i.e., mixed-valence) bimetallocene species are zero. Although Taube and co-workers have used a rather different $\Delta G_e°$ expression for various bipyridine-bridged diruthenium systems,[17] the above relation is considered to be adequate for the present bimetallocene systems.

(16) For example: Brown, G. M.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 883.

(17) Sutton, J. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 3125.

(18) This relationship will probably underestimate H_{AB}, at least for $(Cp_2Co)_2^+$, since this system lies at least on the class II/III borderline; for Class III systems, $H_{AB} = \bar{\nu}_{max}/2$.

(19) For example: Newton, M. D. *J. Phys. Chem.* **1986**, *90*, 3734.

Contribution from the School of Science,
Griffith University, Brisbane, Australia 4111,
and Department of Physical and Inorganic Chemistry,
University of Western Australia, Perth, Australia 6009

Conformational Isomerism in Mixed-Ligand Complexes of 2,2′-Bipyridine and Triphenylphosphine with Copper(I) Halides[†]

Peter F. Barron,[‡] Lutz M. Engelhardt,[§] Peter C. Healy,*[‡] John D. Kildea,[§] and Allan H. White[§]

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Our recent studies on the CP-MAS solid-state ^{31}P NMR spectroscopy of triphenylphosphine (PPh_3) adducts with copper(I)

[†] Lewis-Base Adducts of Group 11 Metal(I) Compounds. 38.

[‡] Griffith University.

[§] University of Western Australia.

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Table I. Solid-State CP-MAS ^{31}P NMR Data for [(PPh$_3$)(bpy)CuX] Compounds[a]

	chem shifts/ppm					line spacings/kHz			
compd	δ_1	δ_2	δ_3	δ_4	$\langle\delta\rangle$	$\Delta\nu_1$	$\Delta\nu_2$	$\Delta\nu_3$	$\Delta\nu_{ij}$
1	5.7	−6.5	−19.1	−31.8	−13	1.48	1.53	1.54	0.06
2	4.7	−7.4	−20.2	−33.1	−14	1.47	1.55	1.57	0.10
3a	3.7	−8.7	−21.9	−35.2	−16	1.50	1.60	1.62	0.12
	9.5	−2.5	−15.7	−29.1	−10	1.46	1.60	1.63	0.17
3b	22.0	9.1	−5.0	−19.5	−2	1.56	1.70	1.76	0.20

[a] δ_i are chemical shift values (±0.4 ppm) with respect to 85% H$_3$PO$_4$ via solid PPh$_3$ ($\delta = -9.9$); $\langle\delta\rangle$ is the average chemical shift for each quartet; $\Delta\nu_i$ is the line spacing in hertz between the four peaks of each quartet; $\Delta\nu_{ij} = \Delta\nu_i(\max) - \Delta\nu_i(\min)$ is defined here as the asymmetry parameter of the quartet.

Table II. Summary of Crystal Data for (PPh$_3$)(bpy)CuX Compounds **1**, **2**, and **3a**

compd	**1** (PPh$_3$)(bpy)CuI	**2** (PPh$_3$)(bpy)CuBr	**3a** (PPh$_3$)(bpy)CuCl
formula	$C_{28}H_{23}CuIN_2P$	$C_{28}H_{23}BrCuN_2P$	$C_{28}H_{23}CuClN_2P$
fw	609.0	562.0	517.5
cryst syst	monoclinic	monoclinic	monoclinic
space group	$C2/c$	$C2/c$	$P2_1/a$
a/Å	34.237 (6)[a]	34.051 (8)	33.77 (2)
b/Å	9.464 (1)	9.366 (1)	9.299 (6)
c/Å	19.081 (4)	18.852 (8)	18.437 (8)
β/deg	124.30 (2)	124.45 (3)	123.06 (4)
V/Å^3	5107 (2)	4958 (2)	4853 (2)
Z	8	8	8
D_c/g cm^{-3}	1.58	1.51	1.42
F(000)	2416	2272	2128
μ_{Mo}/cm^{-1}	22	27	11
specimen dimens/mm	0.04 × 0.25 × 0.08	0.06 × 0.15 × 0.06	0.05 × 0.15 × 0.10
$2\theta_{max}$/deg	50[b]	45	40
N	3936	3227	4306
N_o	3254	2522	2170
ind var	368	368	296
R	0.026	0.033	0.055
R'	0.023	0.033	0.063

[a] Syntex machine with extended counter arm was employed. [b] Data terminated at $h = 28$ due to machine failure.

halides (CuX) have shown that the spectra are sensitive indicators of the number of crystallographically and chemically independent ligands present in the sample;[1] as a result of this work we have been able to isolate several new compounds in the series L$_m$(CuX)$_n$. In extending our studies to the mixed-ligand complexes of triphenylphosphine and 2,2′-bipyridine with copper(I) halides, [(PPh$_3$)(bpy)CuX],[2] we noted, on the basis of the available structural evidence,[3,4] that the spectrum of the chloride showed twice the number of expected lines. Given this unusual result, we decided to complete the structural characterization of this compound together with the iodide and bromide for comparison. The results, reported here, show a novel dichotomy of conformational isomers to be present in the chloride lattice.

Experimental Section

Syntheses. (PPh$_3$)(bpy)CuI (1). A mixture of 0.4 g of CuI, 0.3 g of bpy, and 0.5 g of PPh$_3$ was stirred for 30 min in 50 mL of CH$_3$CN. The starting materials dissolved to give an orange solution from which fine orange crystals of the compound precipitated. Mp: 234–248 °C (lit.[2] mp 225 °C dec). Anal. Calcd for $C_{28}H_{23}ICuN_2P$: C, 55.2; H, 3.8; N, 4.6. Found: C, 55.4; H, 3.8; N, 4.5.

Binding energies (eV): Cu 2p$_{1/2}$, 952.3; Cu 2p$_{3/2}$, 932.5; Cu(L$_3$MM), 915.6; P 2p, 131.0; N 1s, 399.6; I 3d$_{5/2}$, 618.9.

(PPh$_3$)(bpy)CuBr (2). A mixture of 0.3 g of CuBr, 0.3 g of bpy and 0.5 g of PPh$_3$ was stirred for 2 h in 200 mL of CH$_3$CN. The mixture yielded a pale yellow solution from which fine orange crystals of the compound precipitated. Mp: 210–221 °C (lit.[2] mp 193 °C). Anal. Calcd for $C_{28}H_{23}BrCuN_2P$: C, 59.8; H, 4.1; N, 5.0. Found: C, 60.0; H, 4.1; N, 4.9.

Binding energies (eV): Cu 2p$_{1/2}$, 952.1; Cu 2p$_{3/2}$, 932.3; Cu(L$_3$MM), 915.7; P 2p, 131.4; N 1s, 399.3; Br 3d$_{5/2}$, 68.3.

(PPh$_3$)(bpy)CuCl (3a). A 0.2-g sample of CuCl was added to a boiling solution of 0.3 g of bpy and 0.5 g of PPh$_3$ in 20 mL of CH$_3$CN. Fine orange crystals of the complex precipitated from the hot solution. Mp: 195–210 °C (lit.[2] mp 198 °C). Anal. Calcd for $C_{28}H_{23}ClCuN_2P$: C, 65.0; H, 4.5; N, 5.4. Found: C, 65.3, H, 4.5, N, 5.4.

Binding energies (eV): Cu 2p$_{1/2}$, 952.1; Cu 2p$_{3/2}$, 932.3; Cu(L$_3$VV), 915.2; P 2p, 131.1; N 1s, 399.3; Cl 2p, 197.9.

[(PPh$_3$)(bpy)CuCl]·H$_2$O (3b). A reaction similar to the above, carried out at room temperature, resulted in the precipitation of yellow crystals with unit cell dimensions matching those of the previously studied triclinic monohydrate phase.[4] Mp: 195–210 °C. Anal. Calcd for $C_{28}H_{25}ClCuN_2OP$: C, 62.8; H, 4.7; N, 5.2. Found: C, 63.0; H, 4.6; N, 4.5.

Binding energies (eV): Cu 2p$_{1/2}$, 952.2; Cu 2p$_{3/2}$, 932.4; Cu(L$_3$MM), 915.6; P 2p, 131.3; N 1s, 399.3; Cl 2p, 198.2.

In our preparations of the bromide and iodide compounds, we did not observe precipitation of crystals analogous to this yellow triclinic phase.

Spectroscopy. Solid-state ^{31}P NMR spectra of compounds **1**–**3b** were obtained at room temperature on a Bruker CXP-300 spectrometer at 121.47 MHz using ^{1}H–^{31}P cross-polarization with radio frequency fields of 8 and 20 G, respectively, as described previously.[1] Chemical shift and line spacing data are presented in Table I.

X-ray photoelectron spectra were recorded by using a PHI Model 560 spectrometer and Al Kα radiation (1486.6 eV). Samples were ground to a fine powder in a mortar and pestle and dusted as thin films onto double-sided tape. The C 1s line (284.8 eV) from adventitious carbon/ligands was used as an internal standard.

Structure Determinations. A summary of crystal data for compounds **1**–**3a** is presented in Table II. Unique data sets ($h,k,\pm l$) were measured to the specified $2\theta_{max}$ limits on small needles by using Syntex P$\bar{1}$ and Enraf-Nonius CAD-4 four-circle diffractometers (monochromatic Mo Kα radiation sources, $\lambda = 0.7106_9$ Å) in conventional $2\theta/\theta$ scan mode, at 295 K. N independent reflections were measured, N_o with $I > 3\sigma(I)$ being considered "observed", and used in the full-matrix least-squares refinements without absorption correction after solution of the structures by vector methods. $(x, y, z, U_{iso})_H$ were included at idealized values in **3a**; in **1** and **2** $(x, y, z)_H$ were refined. Residuals on $|F|$ at convergence minimizing $\sum w(\Delta|F|^2)$ were R, R'; statistical reflection weights were used, derived from $\sigma^2(I) = \sigma^2(I)_{diff} + 0.0005\sigma^4(I)_{diff}$. Each structure was refined smoothly in the chosen space group with no anomalies with respect to disorder or large thermal envelopes; in **3a**, however, the large body of weak $P2_1/a$ data would only support isotropic thermal parameter refinement for C and N and residuals were higher than those for **1** and **2**. Neutral-atom complex scattering factors were used.[5] No significant extinction effects were observed. Computation used the XTAL83 program system[6] implemented by S. R. Hall on a Perkin-Elmer 3240 computer and the CHEM-X program package (Chemical Designs Ltd.) implemented on a VAX-780 computer. The atom-labeling scheme adopted for each PPh$_3$ ligand was such that the ortho carbon atoms C(m2), where m is

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Table III. Non-Hydrogen Atom Coordinates for $(PPh_3)(bpy)CuI$ (**1**)

atom	*x*	*y*	*z*
I	0.35305 (1)	0.10582 (3)	0.03106 (2)
Cu	0.35718 (2)	0.34961 (5)	0.09744 (3)
P	0.37281 (3)	0.3403 (1)	0.22643 (6)
C(11)	0.3758 (1)	0.5103 (4)	0.2740 (2)
C(12)	0.3878 (1)	0.6288 (4)	0.2483 (3)
C(13)	0.3931 (2)	0.7589 (4)	0.2865 (3)
C(14)	0.3867 (2)	0.7692 (5)	0.3515 (3)
C(15)	0.3745 (2)	0.6539 (5)	0.3774 (3)
C(16)	0.3683 (1)	0.5248 (4)	0.3387 (2)
C(21)	0.4296 (1)	0.2596 (4)	0.3064 (2)
C(22)	0.4471 (2)	0.1551 (5)	0.2810 (3)
C(23)	0.4897 (2)	0.0888 (5)	0.3387 (3)
C(24)	0.5151 (2)	0.1262 (6)	0.4221 (3)
C(25)	0.4986 (2)	0.2296 (6)	0.4478 (3)
C(26)	0.4562 (2)	0.2955 (5)	0.3910 (3)
C(31)	0.3300 (1)	0.2434 (3)	0.2361 (2)
C(32)	0.2830 (1)	0.2811 (4)	0.1823 (2)
C(33)	0.2485 (1)	0.2120 (5)	0.1857 (3)
C(34)	0.2603 (2)	0.1022 (5)	0.2408 (3)
C(35)	0.3065 (2)	0.0628 (4)	0.2939 (3)
C(36)	0.3416 (1)	0.1333 (4)	0.2918 (2)
N	0.3076 (1	0.4932 (3)	0.0116 (2)
C(2)	0.3256 (1)	0.6044 (4)	−0.0057 (2)
C(3)	0.2968 (2)	0.7093 (5)	−0.0610 (3)
C(4)	0.2487 (2)	0.7007 (5)	−0.1003 (3)
C(5)	0.2302 (2)	0.5883 (5)	−0.0834 (3)
C(6)	0.2609 (2)	0.4878 (5)	−0.0275 (3)
N′	0.3999 (1)	0.4876 (3)	0.0830 (2)
C(2′)	0.3777 (1)	0.6053 (4)	0.0384 (2)
C(3′)	0.4021 (2)	0.7184 (5)	0.0354 (3)
C(4′)	0.4506 (2)	0.7084 (6)	0.0788 (4)
C(5′)	0.4730 (2)	0.5891 (6)	0.1215 (4)
C(6′)	0.4466 (2)	0.4801 (5)	0.1232 (3)

Table IV. Non-Hydrogen Atom Coordinates for $(PPh_3)(bpy)CuBr$ (**2**)

atom	*x*	*y*	*z*
Br	0.35271 (2)	0.11856 (5)	0.02842 (3)
Cu	0.35395 (2)	0.34619 (6)	0.09145 (3)
P	0.37158 (4)	0.3414 (1)	0.22327 (7)
C(11)	0.3759 (1)	0.5138 (5)	0.2721 (3)
C(12)	0.3899 (2)	0.6314 (5)	0.2473 (3)
C(13)	0.3967 (2)	0.7626 (6)	0.2863 (4)
C(14)	0.3893 (2)	0.7768 (7)	0.3507 (4)
C(15)	0.3750 (2)	0.6628 (7)	0.3753 (4)
C(16)	0.3680 (2)	0.5324 (6)	0.3361 (3)
C(21)	0.4291 (2)	0.2586 (5)	0.3036 (3)
C(22)	0.4464 (2)	0.1546 (6)	0.2768 (3)
C(23)	0.4897 (2)	0.0882 (7)	0.3353 (4)
C(24)	0.5156 (2)	0.1293 (7)	0.4201 (4)
C(25)	0.4992 (2)	0.2312 (7)	0.4475 (4)
C(26)	0.4557 (2)	0.2969 (6)	0.3900 (3)
C(31)	0.3291 (1)	0.2452 (5)	0.2352 (3)
C(32)	0.2812 (2)	0.2817 (5)	0.1808 (3)
C(33)	0.2470 (2)	0.2118 (6)	0.1846 (3)
C(34)	0.2598 (2)	0.1024 (6)	0.2423 (3)
C(35)	0.3069 (2)	0.0637 (6)	0.2972 (3)
C(36)	0.3411 (2)	0.1365 (5)	0.2937 (3)
N	0.3021 (1)	0.4922 (4)	0.0063 (2)
C(2)	0.3187 (2)	0.6066 (5)	−0.0101 (3)
C(3)	0.2888 (2)	0.7145 (6)	−0.0651 (4)
C(4)	0.2404 (2)	0.7006 (7)	−0.1041 (4)
C(5)	0.2230 (2)	0.5845 (7)	−0.0871 (3)
C(6)	0.2550 (2)	0.4829 (6)	−0.0314 (3)
N′	0.3945 (1)	0.4915 (4)	0.0736 (2)
C(2′)	0.3711 (2)	0.6119 (5)	0.0322 (3)
C(3′)	0.3949 (2)	0.7303 (6)	0.0315 (4)
C(4′)	0.4441 (3)	0.7224 (7)	0.0721 (5)
C(5′)	0.4671 (2)	0.5996 (8)	0.1117 (5)
C(6′)	0.4418 (2)	0.4871 (7)	0.1117 (4)

the ring number, were defined as those atoms above the PC_3 pyramid of the ligand. Where structural data were taken or calculated from published work, the atom labeling was adjusted to conform with this system. Non-hydrogen atom coordinates for **1**, **2**, and **3a** are listed in Tables III–V.

Table V. Non-Hydrogen Atom Parameters for $(PPh_3)(bpy)CuCl$ (**3a**)

atom	*x*	*y*	*z*	10^3U, Å^2
		Molecule 1		
Cl	0.3531 (2)	0.4574 (5)	0.2686 (3)	*a*
Cu	0.35408 (9)	0.2528 (2)	0.3375 (1)	*a*
P	0.3737 (2)	0.2760 (5)	0.4723 (3)	*a*
C(11)	0.3799 (6)	0.108 (2)	0.529 (1)	33 (5)
C(12)	0.3960 (6)	−0.013 (2)	0.507 (1)	48 (6)
C(13)	0.4002 (7)	−0.146 (2)	0.546 (1)	59 (6)
C(14)	0.3883 (7)	−0.156 (2)	0.605 (1)	57 (6)
C(15)	0.3740 (6)	−0.038 (2)	0.631 (1)	49 (6)
C(16)	0.3694 (6)	0.094 (2)	0.592 (1)	40 (6)
C(21)	0.4291 (6)	0.372 (2)	0.549 (1)	29 (5)
C(22)	0.4431 (7)	0.477 (2)	0.514 (1)	62 (6)
C(23)	0.4828 (7)	0.560 (2)	0.568 (1)	67 (7)
C(24)	0.5077 (7)	0.537 (2)	0.656 (1)	57 (6)
C(25)	0.4954 (7)	0.431 (2)	0.693 (1)	58 (6)
C(26)	0.4551 (6)	0.347 (2)	0.637 (1)	41 (6)
C(31)	0.3303 (6)	0.372 (2)	0.483 (1)	29 (5)
C(32)	0.2831 (6)	0.334 (2)	0.428 (1)	35 (5)
C(33)	0.2482 (6)	0.402 (2)	0.431 (1)	50 (6)
C(34)	0.2588 (6)	0.515 (2)	0.488 (1)	42 (6)
C(35)	0.3056 (7)	0.553 (2)	0.544 (1)	58 (6)
C(36)	0.3415 (6)	0.484 (2)	0.541 (1)	43 (5)
N	0.2983 (5)	0.116 (1)	0.2545 (8)	37 (4)
C(2)	0.3132 (6)	−0.006 (2)	0.237 (1)	37 (5)
C(3)	0.2808 (7)	−0.105 (2)	0.178 (1)	60 (6)
C(4)	0.2332 (7)	−0.078 (2)	0.137 (1)	59 (6)
C(5)	0.2172 (6)	0.046 (2)	0.154 (1)	50 (6)
C(6)	0.2524 (7)	0.141 (2)	0.214 (1)	45 (6)
N′	0.3912 (5)	0.085 (1)	0.3183 (8)	42 (4)
C(2′)	0.3636 (6)	−0.030 (2)	0.282 (1)	38 (5)
C(3′)	0.3832 (7)	−0.166 (2)	0.289 (1)	57 (6)
C(4′)	0.4309 (7)	−0.177 (2)	0.333 (1)	71 (7)
C(5′)	0.4600 (7)	−0.061 (2)	0.367 (1)	72 (7)
C(6′)	0.4382 (7)	0.071 (2)	0.358 (1)	63 (7)
		Molecule 2		
Cl	0.3500 (2)	−0.2279 (5)	0.7744 (3)	*a*
Cu	0.35423 (9)	−0.0163 (2)	0.8436 (1)	*a*
P	0.3762 (2)	−0.0355 (5)	0.9807 (3)	*a*
C(11)	0.3852 (6)	−0.220 (2)	1.019 (1)	30 (5)
C(12)	0.4082 (6)	−0.313 (2)	0.995 (1)	40 (5)
C(13)	0.4162 (7)	−0.452 (2)	1.025 (1)	56 (6)
C(14)	0.4020 (7)	−0.501 (2)	1.078 (1)	62 (6)
C(15)	0.3804 (7)	−0.411 (2)	1.105 (1)	54 (6)
C(16)	0.3712 (6)	−0.269 (2)	1.074 (1)	49 (6)
C(21)	0.3342 (6)	0.038 (2)	1.003 (1)	32 (5)
C(22)	0.2862 (6)	0.005 (2)	0.944 (1)	44 (5)
C(23)	0.2507 (7)	0.062 (2)	0.953 (1)	53 (6)
C(24)	0.2636 (6)	0.157 (2)	1.021 (1)	41 (6)
C(25)	0.3106 (6)	0.195 (2)	1.078 (1)	46 (6)
C(26)	0.3466 (6)	0.136 (2)	1.071 (1)	36 (5)
C(31)	0.4321 (6)	0.049 (2)	1.064 (1)	40 (5)
C(32)	0.4497 (7)	0.161 (2)	1.039 (1)	55 (6)
C(33)	0.4913 (7)	0.227 (2)	1.098 (1)	65 (7)
C(34)	0.5163 (7)	0.186 (2)	1.183 (1)	70 (7)
C(35)	0.4993 (7)	0.075 (2)	1.209 (1)	70 (7)
C(36)	0.4582 (6)	0.005 (2)	1.151 (1)	53 (6)
N	0.2979 (5)	0.121 (1)	0.7613 (8)	37 (4)
C(2)	0.3114 (6)	0.242 (2)	0.740 (1)	41 (5)
C(3)	0.2758 (7)	0.334 (2)	0.680 (1)	61 (7)
C(4)	0.2279 (7)	0.308 (2)	0.642 (1)	62 (7)
C(5)	0.2148 (7)	0.185 (2)	0.666 (1)	56 (6)
C(6)	0.2518 (7)	0.097 (2)	0.725 (1)	45 (6)
N′	0.3882 (5)	0.144 (1)	0.8129 (8)	39 (4)
C(2′)	0.3609 (6)	0.261 (2)	0.777 (1)	34 (5)
C(3′)	0.3817 (7)	0.396 (2)	0.777 (1)	57 (6)
C(4′)	0.4294 (7)	0.395 (2)	0.811 (1)	66 (7)
C(5′)	0.4552 (7)	0.280 (2)	0.842 (1)	67 (7)
C(6′)	0.4344 (6)	0.153 (2)	0.844 (1)	48 (6)

[a] Anisotropic (see supplementary Table SUP-VI).

Results and Discussion

The solid-state ^{31}P NMR spectra of compounds **1** and **2** show single, well-resolved quartets with average chemical shift values of −13 and −14 ppm. The line spacings are 1.48–1.54 kHz for

Table VI. Copper and Phosphorus Atom Environments for Compounds **1**–**3b**

	1	**2**	**3a** mol 1	**3a** mol 2	**3b**[4]
		Distances (Å)			
Cu–X	2.597 (1)	2.429 (1)	2.278 (6)	2.307 (6)	2.330 (2)
Cu–P	2.206 (1)	2.202 (1)	2.205 (6)	2.219 (6)	2.180 (2)
Cu–N	2.068 (3)	2.087 (3)	2.09 (1)	2.10 (1)	2.076 (5)
Cu–N′	2.093 (4)	2.097 (4)	2.15 (2)	2.14 (2)	2.087 (6)
P–C(11)	1.822 (5)	1.823 (5)	1.82 (2)	1.81 (2)	1.833 (5)
P–C(21)	1.830 (3)	1.836 (3)	1.85 (2)	1.82 (2)	1.837 (7)
P–C(31)	1.824 (4)	1.823 (4)	1.82 (2)	1.84 (2)	1.831 (8)
		Angles (deg)			
X–Cu–P	114.89 (3)	116.88 (4)	116.8 (2)	116.3 (2)	117.1 (1)
X–Cu–N	113.76 (9)	115.2 (1)	111.5 (4)	111.2 (4)	104.5 (2)
X–Cu–N′	109.9 (1)	108.8 (1)	110.3 (5)	109.3 (5)	102.9 (5)
P–Cu–N	118.9 (1)	117.0 (1)	118.8 (5)	118.7 (5)	123.2 (1)
P–Cu–N′	115.1 (1)	114.2 (1)	114.4 (4)	117.5 (4)	122.8 (2)
N–Cu–N′	79.0 (1)	78.3 (2)	79.1 (6)	77.7 (6)	79.2 (2)
Cu–P–C(11)	115.5 (1)	116.3 (2)	115.4 (6)	113.4 (6)	113.9 (2)
Cu–P–C(21)	115.0 (2)	114.9 (2)	118.0 (8)	114.3 (5)	103.5 (2)
Cu–P–C(31)	115.4 (1)	114.8 (1)	114.2 (5)	118.1 (8)	116.7 (2)
C(11)–P–C(21)	102.6 (2)	102.3 (2)	102.8 (7)	104.9 (10)	104.2 (3)
C(21)–P–C(31)	104.0 (2)	103.9 (2)	102.6 (8)	102.8 (9)	103.5 (3)
C(11)–P–C(31)	102.5 (1)	102.6 (3)	101.6 (10)	101.6 (7)	103.5 (3)

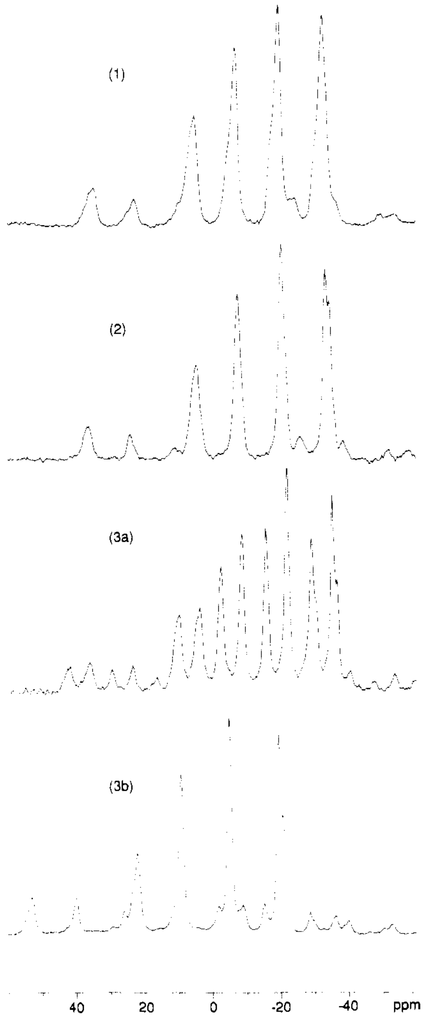

Figure 1. CP-MAS solid-state ^{31}P NMR spectra of the monoclinic phase of $(PPh_3)(bpy)CuX$ for **1**–**3b**. The spinning side bands observed on either side of the main signal indicate the existence of ^{31}P chemical shift anisotropy. Small satellite peaks observed on the main high-field peaks are attributable to resolution of the ^{65}Cu isotope peaks. The spectrum of **3b** shows evidence of the presence of a small quantity of **3a** in the sample used for analysis.

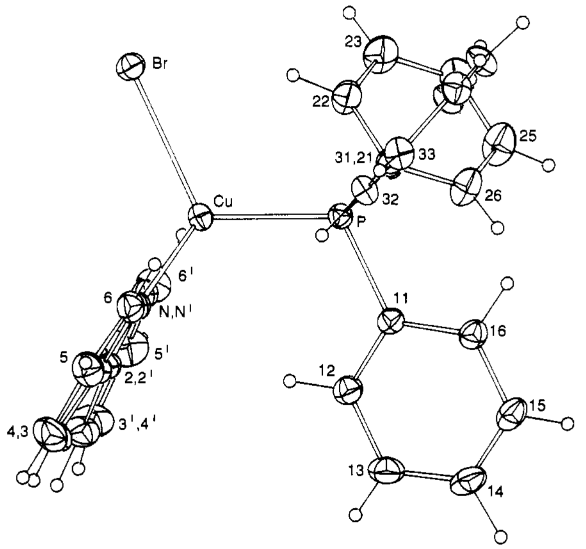

Figure 2. A single molecule of $[(PPh_3)(bpy)CuBr]$ (**2**) projected normal to the X–Cu–P plane. Hydrogen atoms have a arbitrary radius of 0.1 Å. Thermal envelopes are at the 20% probability level here and below. The iodide (**1**) has the same conformation.

1 and 1.47–1.57 kHz for **2** (Figure 1, Table I). These values are marginally smaller than the average value of 1.70 kHz calculated from data recorded for other copper(I) complexes with a single coordinated PPh_3 ligand. For comparison, compounds with two and three ligands have average line spacings of 1.25 and 0.93 kHz, respectively.[1] The small differences in line spacing of ca. 100 Hz are consistent with the pseudotetrahedral copper(I) geometry expected for this type of compound. In contrast, the spectra of the chloride compound, **3a**, showed two quartets with average chemical shifts of −16 and −10 ppm (Figure 1, Table I). The line spacings of 1.50–1.62 and 1.46–1.63 kHz are, however, quite similar to those of **1** and **2**. The spectrum of the hydrated chloride compound, **3b**, again shows a single quartet, but this is shifted significantly downfield and the line spacings are marginally greater.

The unit cell dimensions of **1**, **2**, and **3a** each show a lattice based on a monoclinic cell with $a \sim 34$ Å, $b \sim 9.5$ Å, $c \sim 18.5$ Å, and $\beta \sim 124°$. However, whereas both **1** and **2** crystallize in the space group $C2/c$ with one independent molecule in the asymmetric unit, **3a** crystallizes in space group $P2_1/a$ with two independent molecules. Surprisingly, each of these molecules is able to adopt different conformational structures without significantly changing the overall cell dimensions. In molecule 1, the PPh_3 ligand is staggered with respect to the Cu–Cl bond

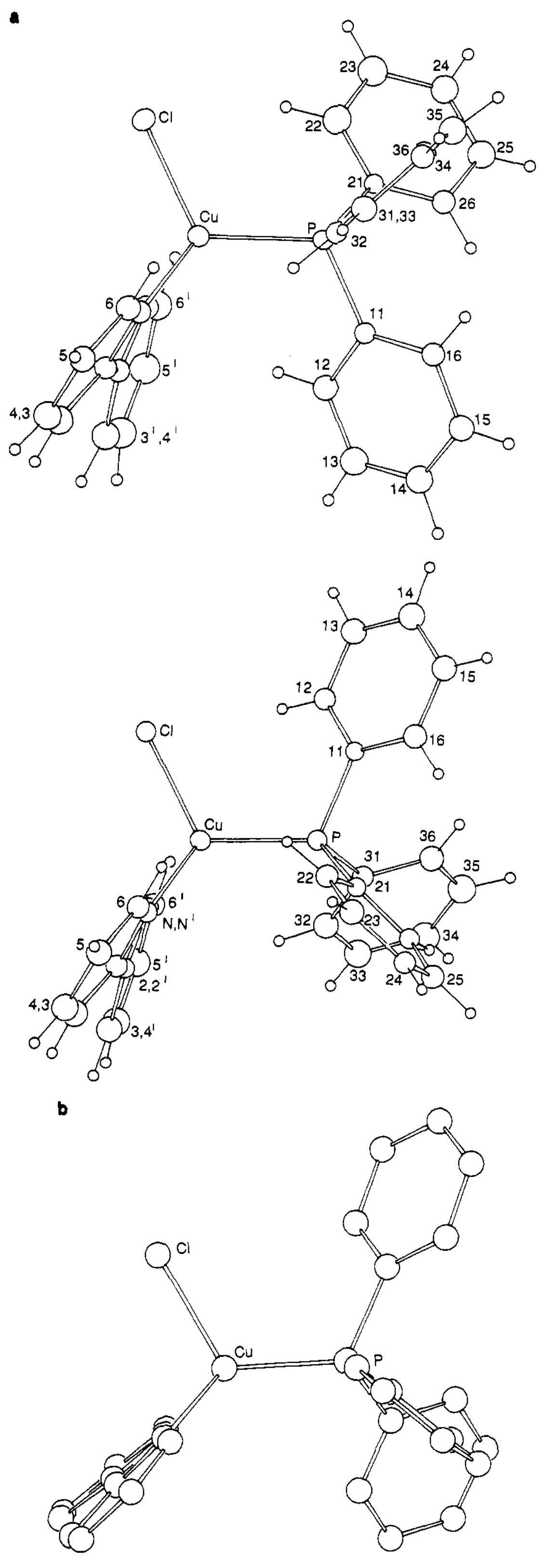

Figure 3. (a) Upper, lower parts: Similar projections of molecules 1 and 2 of [$(PPh_3)(bpy)CuCl$] (**3a**) showing the different conformations of the two molecules. ((Equivalent) isotropic thermal envelopes are shown in parts a and b.) (b) A similar projection of [$(PPh_3)(bpy)CuCl$] (**3b**) taken from the data of its monohydrate structure.[4]

whereas, in molecule 2, it is eclipsed (Figures 2–4). For each conformer, the intra- and intermolecular X···H and N···H contact distances are similar, ranging between 2.7 and 3.2 Å; and the triphenylphosphine and bipyridine ligands presumably vary their conformational structures in order to accommodate the changes in lattice forces. The dihedral angles between the two rings of

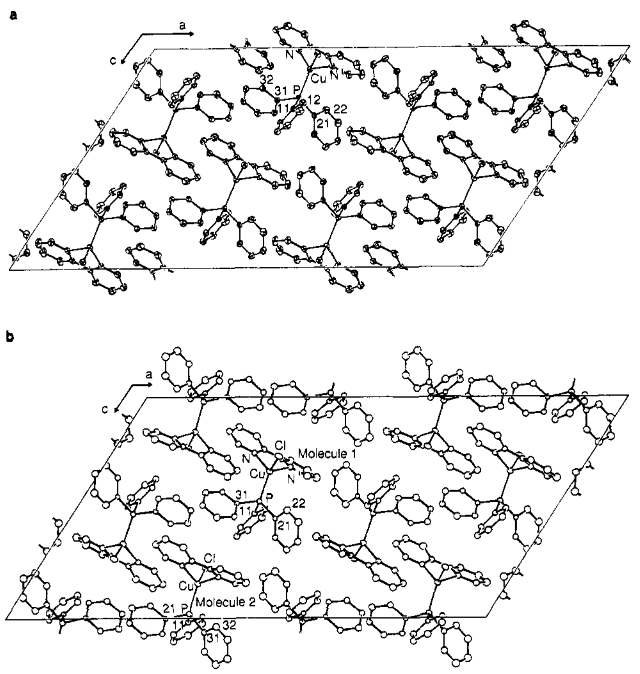

Figure 4. (a) Unit cell contents of [$(PPh_3)(bpy)CuBr$] (**2**) projected down b (space group $C2/c$). (b) Unit cell contents of [$(PPh_3)(bpy)CuCl$] (**3a**) projected down b. The cell symmetry is now $P2_1/a$ and is shown in relation to that of Figure 4a.

the bpy ligand are 7.4° for **1**, 9.2° for **2**, 18.6 and 17.7° for **3a**, and 5.7° for **3b**. Similarly, the three phenyl rings in the PPh_3 ligand adopt Cu–P–C(m1)–C(m2) torsion angles ranging between 26 and 52°.

The PN_2CuX core geometries for the compounds are detailed in Table VI. Cu–N distances range from 2.068 (3) to 2.097 (4) Å for **1**, **2**, and **3b** and from 2.09 (1) to 2.15 (1) Å for **3a**. It is plausible to argue that, for this latter structure, the increase in both the Cu–N bond lengths and the differences between them is a consequence of the asymmetric intra- and intermolecular nonbonding interactions that are present. For general comparison, in the α and β phases of $(PPh_3)(phen)CuBH_4$, Cu–N distances are 2.12 (1) and 2.149 (7) Å and 2.15 (1) and 2.139 (5) Å, respectively.[7] The Cu–Cl distances in the chloride structures vary significantly. They are 2.278 (6) Å for molecule 1 of **3a**, where the phosphine is staggered with respect to the Cu–Cl bond, 2.307 (6) Å for molecule 2, where the phosphine is eclipsed, and 2.330 (2) Å in **3b**, where the water of solvation is strongly hydrogen bonded to the chloride.[4]

A characteristic feature of the structural chemistry of monomeric complexes of copper(I) halides containing triphenylphosphine is the invariance of the Cu–P bond length to changes in the halide,[1] and in the present series of compounds the Cu–P distances again span only a small range of values. For **1**–**3a**, these distances range between 2.202 (1) and 2.219 (6) Å, with both extremes of the range being defined by the two molecules of **3a** (Table VI) with a slightly shorter distance of 2.180 (2) Å in **3b**. This shorter Cu–P distance is consistent with the slightly longer Cu–Cl distance and also with the marginally greater ^{31}P NMR line spacings that are observed in this compound. The invariance of the Cu–P bond length with halide has been extended to include [$(PPh_3)_2CuBH_4$],[8] and for the present class of compounds, Cu–P distances of 2.205 (2) and 2.227 (2) Å reported for the α and β forms of [$(PPh_3)(phen)CuBH_4$][7] are also remarkably similar, despite the change in the bidentate ligand.

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Registry No. 1, 25753-82-6; **2**, 25753-81-5; **3a**, 25753-80-4.

Supplementary Material Available: Tables SUP-I–SUP-X, listing non-hydrogen thermal parameters, the derived hydrogen atom positions, and ligand non-hydrogen geometries (12 pages); tables of calculated and observed structure factors (35 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
New Mexico State University,
Las Cruces, New Mexico 88003-0001

Kinetics of Interaction of Copper Ion with Four Diaza-Crown-Alkanoic Acid Complexes

Stanislaw P. Kasprzyk[1] and Ralph G. Wilkins*

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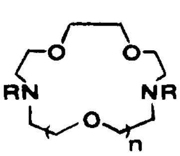
Thermodynamic considerations have dominated the subject of metal ion complexing of macrocyclic ligands, as an examination of a recent comprehensive review of cation–macrocycle interaction clearly shows.[2] Increasing attention is however being given to the kinetic aspects of complex formation with porphyrins,[3] crown ethers,[4] cryptands,[5] and aza macrocycles.[6] We are however still far from understanding the general details of ligand conformational changes necessary to present the macrocycle in a correct orientation before and during metal binding. An interesting and as yet little explored aspect is the complexing of macrocycles with pendent arms capable of coordinating.[7,8]

We have recently studied the kinetics of formation of complexes of metal ions with the macrocyclic ligands 1,4,7,10-tetraazacyclododecane-*N,N′,N″,N‴*-tetraacetate (DOTA) and 1,4,8,11-tetraazacyclotetradecane-*N,N′,N″,N‴*-tetraacetate (TETA).[8] For a number of metal ions, including Cu^{2+}, the kinetic data conformed to the rapid formation of an adduct, which either converted to the final complex or acted as a "dead-end" complex, in which case the reactants interacted separately by a second-order process to give the final complex.

In this note we report the kinetics of the complexing of copper ion by the four macrocycles 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane-7,16-diacetic acid (Ia), -7,16-di-α-propionic acid (Ib), and -7-acetic acid (Ic) and 1,4,10-trioxa-7,13-diazacyclopentadecane-7,13-diacetic acid (Id). One and two pendent carboxylate residues as well as 15- and 18-membered macrocycles are presented to the metal ion by this selection of ligands. The structures of the solid Cu^{2+} complexes of Ia and Ib have been solved.[9,10] The copper is coordinated by the two amino acid residues in a transplanar configuration. The copper is also contained in the macrocycle ring with axial binding to two ether oxygens. It is reasonable to suppose that these structures persist in solution. Models show that the smaller 15-membered macrocycle ring present in Id brings the ether oxygens closer to the copper than does the 18-membered counterpart in Ia, and this may account[11,12] for the enhanced Cu(II) formation constant for Id ($10^{16.0}$)[11] over that for Ia ($10^{14.5}$).[13] With Ic in the solid state, coordination with Cu^{2+} is via the two N's and the one carboxylate sidearm of the macrocycle, as well as via O(4) and O(13) ether oxygens.[14] The effect of pendent arms, pH, and ring size on the kinetic characteristics can therefore be assessed.



I

Ia, R = R^1 = CH$_2$COOH, n = 2
Ib, R = R^1 = CH(CH$_3$)COOH, n = 2
Ic, R = CH$_2$COOH, R^1 = H, n = 2
Id, R = R^1 = CH$_2$COOH, n = 1

Experimental Section

Ligands Ia, Ib, and Id were prepared by literature methods.[12,15] Ligand Ic was prepared as follows: A 10-mmol quantity of chloroacetic acid in 25 mL of water was adjusted to pH 9.5 with 4 M NaOH. The solution was added dropwise over a period of 4 h to a boiling solution of 15 mmol of Kryptofix 22 (50% excess) in 20 mL of water. The mixture was refluxed for 10 h, and then it was adjusted to pH 12 with 4 M NaOH. The solution was extracted with chloroform (3 × 50 mL) to remove any unreacted Kryptofix 22. The aqueous layer was concentrated in vacuo and purified by passing through an ion-exchange column (Amberlite IR-120). The product was recrystallized from ethanol and dried in vacuo over P_4O_{10} (yield 70%). Anal. Calcd for $C_{14}H_{28}N_2O_6\cdot H_2O$: C, 49.70; H, 8.88; N, 8.28. Found: C, 49.45; H, 8.86; N, 8.28. These analyses were carried out at the Institute of Organic Chemistry.[1]

The compound appears not to have been described previously, although it was used, unpurified, as an intermediate in the preparation of an unsymmetrical N,N′-disubstituted Kryptofix 22 derivative.[16]

All studies were carried out at 25 °C and at an ionic strength of 0.1 M maintained with a lightly buffered sodium acetate/acetic acid and NaCl mixture. Most of the reactions were carried out at pH 3.75–4.75, with copper ion in excess (1–10 mM) over ligand (0.1–0.2 mM) and with monitoring at 330 nm. The kinetic data were independent of the concentration of the species in deficiency and of a change of wavelength from 300–350 to 600 nm (small absorbance change). A change of concentration of acetate ion from 0.01 to 0.05 M had no effect on the rate, indicating that the reactivity of the copper acetate species was similar to that of the aqua ion. The experiments were carried out in a Gibson-Dionex stopped-flow apparatus interfaced with an OLIS data collection system. Each rate constant quoted in Table I is the mean of several determinations and can be considered to have ±5% accuracy.

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(1) Present address: Institute of Organic Chemistry, Polish Academy of Sciences, ul. Kasprzaka 44, 01-224 Warszawa, Poland.

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