Table II. Atomic Coordinates ($\times 10^5$ for Pt, I, and P; $\times 10^4$ for K, O, and C) and Equivalent Isotropic Temperature Factors[a] ($\text{Å}^2 \times 10^4$ for Pt, I, and P; $\text{Å}^2 \times 10^3$ for K, O, and C)

atom	Wyckoff position	site symm	x	y	z	U_{eq}
Pt	4(e)	$4mm$	0	0	8811 (4)	176 (1)
I	4(e)	$4mm$	0	0	26647 (16)	452 (6)[b]
P	16(n)	m	0	24670 (19)	9302 (14)	248 (5)
O(1)	32(o)	1	1297 (4)	3138 (5)	1345 (4)	50 (2)
O(2)	8(i)	mm	0	3144 (12)	0	103 (7)
C	4(e)	$4mm$	0	0	2260 (24)	31 (6)[b,c]
K(1)	4(d)	$\bar{4}m2$	0	5000	2500	36 (1)
K(2)	8(j)	mm ·	2600 (7)	5000	0	41 (2)[b]
Ow	8(j)	mm	5000	3210 (23)	0	61 (9)[b]

[a] Calculated as one-third of the trace of the orthogonalized U_{ij} matrix.　　[b] Half site occupancy.　　[c] Varied isotropically.

effect of the bridging ligand L.[10] However, the observed lengthening (ca. 0.09 Å) of the Pt–Pt distance in $[Pt_2(pop)_4CH_3I]^{4-}$ relative to that in $[Pt_2(pop)_4Cl_2]^{4-}$ clearly indicates that a strong trans influence is exerted by the methyl and iodide ligands. In accordance with this, the $E(d\sigma \rightarrow d\sigma^*)$ transition has been found to be substantially red shifted in going from $[Pt_2(pop)_4Cl_2]^{4-}$ to $[Pt_2(pop)_4CH_3I]^{4-}$.

The Pt–I bond distance in the present complex [2.816(3) Å] lies between that of a Pt–I single bond (ca. 2.64–2.68 Å)[16–18] and those observed in $[Pt_2(S_2CMe)_4I]$ [2.975 (2) and 2.981 (3) Å].[15] It is, in fact, comparable to the shorter of the two alternating metal–halide distances along the chain in such Wolfram's salt analogous as $[Pt(dapn)_2][Pt(dapn)_2I_2](ClO_4)_4$ [2.791 (8) and 3.036 (8) Å][19] and $[Pt(dapn)_2][Pt(dapn)_2I_2]I_4$ [2.815 (2) and 2.995 (2) Å],[20] where dapn stands for 1,2-diaminopropane. The Pt–C bond of 2.18 (3) Å is also significantly longer than most Pt^{II}–C σ-bonds (ca. 2.08 Å[21]) and compares well with the Pt^{IV}–C distance of 2.15 (1) Å in $PtI_2(CH_2)_4(PMe_2Ph)_2$.[8] The observed lengthening of the Pt–CH_3, Pt–I, and Pt–Pt bonds in $[Pt_2(pop)_4CH_3I]^{4-}$ is consistent with axial σ electronic delocalization and suggests further that the Pt^{III} species will undergo reductive elimination relatively easily.

The pronounced anisotropic thermal motion of O(1) and O(2) (Figure 1) is probably more representative of minor positional disorder imposed by the required $4/mmm$ symmetry of $[Pt_2(pop)_4CH_3I]^{4-}$ anion rather than a large vibrational effect. Allowing for the statistical equivalence of the P=O and P—OH groups, the measured dimensions of the diphosphite ligand and the Pt–P distance (Figure 1) are in reasonable agreement with those observed in the series $[Pt_2(pop)_4]^{4-}$, $[Pt_2(pop)_4Br]^{4-}$, and $[Pt_2(pop)_4Cl_2]^{4-}$.[10,22]

The potassium ions, which occupy two different special positions iin the unit cell, play a critical role in consolidating the crystal packing through ionic interactions with both the diphosphite and water oxygen atoms. Atom K(1) is located at a site of symmetry $\bar{4}m2$, being surrounded by eight symmetry-equivalent O(1) atoms arranged in two rectangles normal to the c axis [K(1)···O(1) = 2.819(5) Å].[23] Atom K(2) half-occupies a site of symmetry mm; it is also eight-coordinate, but the primary coordination sphere is less regular

and comprises four interactions with O(1) at 3.024 (6) Å, two with O(2) at 3.027 (8) Å, and two with Ow at 2.837 (14) Å.[24] Unlike the water molecule in $K_4[Pt_2(pop)_4Cl_2]\cdot 2H_2O$,[10] which is hydrogen bonded to diphosphite ions, the 2-fold disordered Ow atom in $K_4[Pt_2(pop)_4CH_3I]\cdot 2H_2O$ serves only as a bridging ligand between two symmetry-related K(2) atoms.

It is of interest to compare the crystal structures of the series of binuclear platinum diphosphite complexes $K_4[Pt_2(pop)_4]\cdot 2H_2O$, $K_4[Pt_2(pop)_4Br]\cdot 2H_2O$, $K_4[Pt_2(pop)_4Cl_2]\cdot 2H_2O$, and $K_4[Pt_2(pop)_4CH_3I]\cdot 2H_2O$. In the first two complexes (same space group, $P4/mbm$), the roughly cylindrical $Pt_2(pop)_4$ "barrels" stack in columns parallel to the c axis, whereas no such end-to-end stacking occurs in the dichloro complex (space group $P\bar{1}$). In $K_4[Pt_2(pop)_4CH_3I]\cdot 2H_2O$, the noninteracting $Pt_2(pop)_4$ barrels are arranged in columns along the c direction, with a much increased interbarrel gap necessitated by the I lattice centering. It is noteworthy that the a axis of $K_4[Pt_2(pop)_4CH_3I]\cdot 2H_2O$ is approximately equal to half of the face diagonal of the base of the unit cell in either K_4-$[Pt_2(pop)_4]\cdot 2H_2O$ or $K_4[Pt_2(pop)_4Br]\cdot 2H_2O$ (see Figure 1 of ref 10), indicating very similar lateral packing of the columns in the three tetragonal crystalline compounds.

Supplementary Material Available: Listings of structure factors (Table III) and anisotropic thermal parameters (Table IV) (7 pages). Ordering information is given on any current masthead page.

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(24) Symmetry-generated O(1) positions at (x, y, z), $(x, y, -z)$, $(x, 1-y, z)$, and $(x, 1-y, -z)$; O(2) positions at (x, y, z) and $(x, 1-y, z)$; Ow positions at (x, y, z) and $(x, 1-y, z)$.

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^{63}Cu NMR Studies of Copper(I) Complexes. Relationship between ^{63}Cu Chemical Shift and Metal–Ligand Binding

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Copper(I) complexes, which occur naturally in the active sites of copper proteins,[1] and are utilized in organic synthesis

Table I. Observed ^{63}Cu NMR Shifts^a of [CuL$_4$]ClO$_4$

L	solvent	$\Delta\delta$ shifts^b	$\Delta\nu_{1/2}$ line width, Hz^c
CH$_3$CN	CH$_3$CN	0	500
C$_2$H$_5$CN	C$_2$H$_5$CN	13	950
4-CH$_3$py	4-CH$_3$py	100	2440
3-CH$_3$py	3-CH$_3$py	108	2830
py	py	110	1100
CN^{-d}	H$_2$O	499	940
C$_4$H$_9$NC	C$_4$H$_9$NC	451	4000
C$_6$H$_{11}$NC	C$_6$H$_{11}$NC	468	880
4-CH$_3$C$_6$H$_4$NC	4-CH$_3$C$_6$H$_4$NC	547	320
C$_6$H$_5$NC	C$_6$H$_5$NC	549	300
4-ClC$_6$H$_4$NC	CH$_2$Cl$_2$^{e}	553	230

^{a} Observed at 25 °C. ^{b} Referenced against 0.05 M CH$_3$CN solution of [Cu(CH$_3$CN)$_4$]ClO$_4$. ^{c} At half-height. ^{d} [KCN]/[CuCN] = 5. ^{e} [RNC]/[Cu] = 200.

as catalysts,[2] have few spectroscopic properties such as a visible absorption ascribed to d–d transition and electron spin resonance spectra. This is due to their d^{10} configuration, characteristic of diamagnetism. ^{1}H and ^{13}C NMR spectroscopy has been proved to be a useful tool for the characterization of copper(I) complexes in solution.[3] The recent advent of multinuclear magnetic resonance instruments enables one to observe ^{63}Cu NMR signals of some typical copper(I) complexes.[4] The metal–ligand bonding in question has so far been indirectly investigated with the aid of the IR stretching frequencies[5] of coordinated carbon monoxide and nitric acid on the basis of "trans influence" in the ternary metal complexes. In copper(I) complexes, ^{63}Cu NMR is the most relevant method to inquire into the metal–ligand bonding because it provides direct information about the copper itself coordinated by the ligand.

The natural abundance of the ^{63}Cu nucleus is 69.09%, and its resonance frequency is relatively high among the observable metal nuclei, leading to the satisfactory receptivity of 365 with reference to ^{13}C. The spin of the ^{63}Cu nucleus is $^3/_2$. It is well-known[6] that a nucleus of spin I higher than $^1/_2$ often gives a broad resonance line due to the quadrupolar relaxation mechanism, which depends on the coordination environment[6] of the metal center. Fortunately, most copper(I) complexes prefer a tetrahedral form, which provides a relatively sharp resonance line. This work is concerned with the observation of ^{63}Cu NMR spectra of some copper(I) complexes and the exploration of the origin of the ^{63}Cu chemical shift.

Experimental Section

Materials. [Cu(CH$_3$CN)$_4$]ClO$_4$ was utilized as a starting copper(I) source.[7] Isocyanides have been synthesized according to the literature.[8] Pyridines were commercially available and purified before use. The copper(I) complexes were prepared at 25 °C under a highly purified

nitrogen atmosphere.[3] The resultant 0.10 M solution of [CuL$_4$]ClO$_4$ was obtained by the addition of 5 mL of a ligand to [Cu(CH$_3$CN)$_4$]ClO$_4$ (0.164 g). [Cu(C$_2$H$_5$CN)$_4$]ClO$_4$ was prepared[9] from CuCl$_2$(H$_2$O)$_2$/Cu/C$_2$H$_5$CN to avoid the coordination of CH$_3$CN.

Measurement of ^{63}Cu NMR Spectra. ^{63}Cu NMR spectra were recorded on ligand solutions contained in spinning tubes (outside diameter 10 mm) on a JOEL FX 200 multinuclear spectrometer operated in the pulsed Fourier transform mode at an observing frequency of 52.92 MHz (4.7 T). For most samples the rate of quadrupolar-induced longitudinal relaxation was sufficient to permit a pulse repetition rate of 5–9 pulses s^{-1} or faster, and normally 500–1000 transients (total time 60–200 s) gave a satisfactory signal-to-noise ratio in the transformed spectra. Typically a spectral width of 40 kHz was used, and free induction decay was acquired in about 8K data points. The ^{63}Cu chemical shifts in Table I are given relative to a 50 mM solution of [Cu(CH$_3$CN)$_4$]ClO$_4$ in acetonitrile at 25 °C: $\Delta\delta = [\nu_{sample} - \nu_{ref}]/\nu_{ref}$.

Results and Discussion

Two- or three-coordinate copper(I) complexes, because of their low symmetry around the copper center, give quite a broad resonance line as a consequence of the promotion of the quadrupole relaxation rate.[10] Four-coordinate copper(I) complexes have a structure close to cubic symmetry, giving a narrower resonance line and thus making its detection easy. The tetrahedral binary copper(I) complexes suffice for the primary purpose of gaining the correlation of the metal–ligand bonding with ^{63}Cu chemical shift. Hence, the large excess concentration of ligand, usually as a solvent, is utilized in order to form the four-coordination copper(I) complex (CuL$_4$) completely. The observed chemical shift and line width at half-height are presented in Table I.

The line widths in Table I fall within 4 kHz. Copper(I) complexes of aryl isocyanides give the smallest line width,[11] which is also reproduced in acetone solutions containing a low concentration of ligand ([RNC]/[Cu] = 4–10). The stability constant of isocyanide is such that the conversion to CuL$_4$ is quite quantitative. On the other hand, when the ligand is diluted with acetone, the resonance line of copper(I) complexes of pyridines and nitriles undergoes line-broadening without a bias in the position. This fact reveals the presence of equilibria of CuL$_4$ with another complex of lower symmetry. Hence, the effect of line broadening among these copper(I) complexes studied here is likely ascribed to chemical equilibria exchange[4b,10] between tetrahedrally coordinated species and species with lower symmetry and coordination numbers.

The range of ^{63}Cu chemical shifts is ca. 600 ppm, indicative of satisfactory sensitivity to the metal–ligand bonding in spite of the closed-d-shell system.[6] It should be emphasized in Table I that the following increasing order in downfield shift is obtained, RCN < py < CN$^-$ ≈ RNC. This order corresponds well with that in π-acceptor capability, which was obtained from IR spectra[5] of mixed-ligand metal complexes.

We are in a position to examine ^{63}Cu chemical shifts of copper(I) complexes coordinated to homologous ligands. First, among the series of pyridine complexes[12] the following downward trend for $\Delta\delta$ is found: 4-Me-py < 3-Me-py < py.

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(11) Because isocyanide is quite a good π acceptor,[15,16] the narrowest line width in the case of isocyanides is not accounted for by the view[10a] that the line broadening is accelerated by the π-acceptor properties of ligands as documented for the increasing line width within the series CH$_3$CN < py < bpy < phen. Bpy and phen are bidentate ligands, and their copper(I) complexes encounter some deviation from tetrahedral geometry in comparison with that for a monodentate ligand. Hence, the line broadening occurring in the case of bpy and phen may be attributed to the geometry around copper(I).
(12) Various pyridine derivatives, i.e. 4-cyano-, 4-acetyl-, 4-chloro-, and 3-chloropyridine, were prepared to obtain the ^{63}Cu NMR spectra. Their resonance lines are broadened out and cannot be detected.
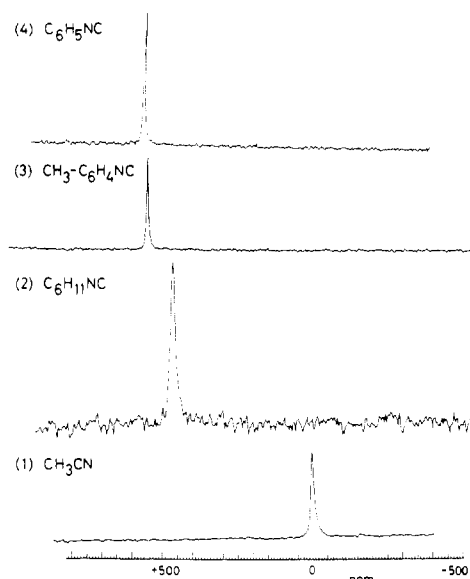
Figure 1. ^{63}Cu NMR spectra at 25 °C of [Cu(CH$_3$CN)$_4$]ClO$_4$ (1), [Cu(C$_6$H$_{11}$NC)$_4$]ClO$_4$ (2), [Cu(CH$_3$C$_6$H$_4$NC)$_4$]ClO$_4$ (3), and [Cu-(C$_6$H$_5$NC)$_4$]ClO$_4$ (4).

The apparent increase antiparallels the increase of the ligand basicity:[13] 4-Me-py, pK_a = 6.03; 3-Me-py, pK_a = 5.68; py, pK_a = 5.23. We have demonstrated[3b,14] that ligands having good π-acceptor capability cause the metal to ligand charge-transfer (MLCT) band, L←Cu, to shift to longer wavelength. The copper(I) complexes of these pyridines give MLCT bands in the order 319 nm (4-Me-py) < 330 nm (3-Me-py and py). On this basis, the increasing order of π-acceptor capability is 4-Me-py < 3-Me-py ≈ py, indicative of good agreement with that in ^{63}Cu chemical shift. The dominant factor influencing the chemical shift of the ^{63}Cu NMR signal is linked to the π-acceptor properties of the pyridine nitrogen.

Second, the substituent effect on Δδ is estimated for copper(I) complexes of isocyanides as well as cyanide ion. The ^{63}Cu NMR spectra of [Cu(RNC)$_4$]ClO$_4$ are first observed here, and some of them are shown in Figure 1. A single sharp line is observed with quite a large downfield shift ranging 451–553 ppm. Table I exhibits that the downfield shift for the aryl isocyanide is greater than that for the alkyl isocyanide, which is also accounted for by the π-acceptor properties because the π-acceptor capability of aryl isocyanide is superior to that of alkyl isocyanide.[15] The IR stretching frequencies and ^{13}C NMR shift of the NC group of the aryl isocyanides have shown that there is minor electronic coupling[15,17] between the NC and the phenyl group. The ^{63}Cu NMR spectra, however, distinguish well between substituents attached to the 4-position of the phenyl isocyanide. With Me and Cl the observed shift varies ca. 6 ppm. The cyanide ion also shows a downfield shift[18] comparable with that of isocyanides. On the other hand, nitrile complexes of copper(I), Cu(RCN)$_4$ (R = CH$_3$ and C$_2$H$_5$), show a considerable upfield shift, attributable to the poor π-acceptor capability of RCN.[19] Table I reveals that propionitrile experiences a downfield shift 13

ppm more than that in the case of acetonitrile, indicative of the sensitiveness of the ^{36}Cu shift.

In conclusion, the ^{63}Cu resonances are deshielded with an increase in π-acceptor capability of the coordinated ligand. The substituent effect on the metal–ligand bonding in homologous series is reflected well by ^{63}Cu NMR spectra.

Registry No. [Cu(CH$_3$CN)$_4$]ClO$_4$, 14057-91-1; [Cu(C$_2$H$_5$C-N)$_4$]ClO$_4$, 15170-21-5; [Cu(4-CH$_3$py)$_4$]ClO$_4$, 35232-25-8; [Cu(3-CH$_3$py)$_4$]ClO$_4$, 93110-83-9; [Cu(py)$_4$]ClO$_4$, 21465-66-7; [Cu(CN)$_4$]$^{3-}$, 19441-11-3; [Cu(C$_4$H$_9$NC)$_4$]ClO$_4$, 93110-85-1; [Cu(C$_6$H$_{11}$NC)$_4$]-ClO$_4$, 93110-87-3; [Cu(4-MeC$_6$H$_4$NC)$_4$]ClO$_4$, 77744-79-7; [Cu-(C$_6$H$_5$NC)$_4$]ClO$_4$, 93110-88-4; [Cu(4-ClC$_6$H$_4$NC)$_4$]ClO$_4$, 93110-89-5; ^{63}Cu, 14191-84-5.

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Detailed Correlations between the Ligand-to-Metal Charge-Transfer (LMCT) Spectra of Copper(II) and Ruthenium(III) Imidazoles and Imidazolates. Electronic Structures of Carbon-Bound Ruthenium(III) Imidazoles and Imidazolates

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The common occurrence of histidine imidazole donors in numerous copper (and iron) proteins has prompted many studies of metal ion–imidazole interactions. We have been studying the imidazole → Cu(II) ligand-to-metal charge-transfer (LMCT) absorptions of model Cu(II) complexes in order to identify and better understand corresponding absorptions in the spectra of Cu(II) proteins.[1,2] Our previous studies have employed Cu(II)–tetrakis (imidazole) systems, and we have been searching for simpler model complexes that possess only one imidazole in order to bypass possible electronic and steric interactions among the imidazole units. We are concerned that such interactions may be partly responsible for the currently inexplicable differences in intensities between the LMCT absorptions of solid-state and solution Cu(imidazole)$_4^{2+}$ chromophores.[1,2] The possible motion of the imidazole ligands around the Cu–N axes makes it difficult to correlate the geometric as well as electronic structures of these complexes in the solid-state and solution phases. Moreover, the LMCT absorptions of Cu(II)–imidazolate chromophores are poorly characterized. Little is known aside from the observation that Cu(II)–imidazolate chromophores exhibit a LMCT absorption in the near-UV region that is not present in the spectra of reference Cu(II)–imidazole complexes.[2] Furthermore, the systems studied were polynuclear imidazolate-bridged Cu(II) complexes, and their suitability as spectroscopic models for the imidazolate-bridged Cu(II)/Zn(II) unit of superoxide dismutase must be suspect.

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