effect of the bridging ligand L. However, the observed 
lengthening (ca. 0.09 Å) of the Pt–Pt distance in [Pt2-
(pop)4CH3I]2+ relative to that in [Pt2(pop)4Cl]2+ clearly 
indicates that a strong trans influence is exerted by the 
iodide ligands. In accordance with this, the E(02 → O*) 
transition has been found to be substantially red shifted 
going from [Pt2(pop)4Cl2]2+ to [Pt2(pop)4CH3I]2+.

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 [Pt2(S2CMe2)2]I2 [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)2I2](ClO4)
4 [2.791 (8) and 3.036 (8) Å]19 and [Pt(dapn)2][Pt(dapn)2I2]
4 [2.815 (2) and 2.995 (2) Å],20 where dop stands for 1,2-
diaminopropane. The Pt–C bond of 2.18 (3) Å is also 
significantly longer than those of Pt–C–O bonds (ca. 2.08 Å)21 
and compares well with the PtIV–C distance of 2.15 (1) Å in 
Pt12(CH2)4(PMe2Ph)2.8 The observed lengthening of the 
Pt–CH3, Pt–I, and Pt–Pt bonds in [Pt2(pop)4CH3I]2+ is con-
trasted with axial 

Pt1I1

the face diagonal of the base of the unit cell in either K4-
[Pt2(pop)4CH3I]2+ or K4[Pt2(pop)4Br]2H2O (see Figure 1) of 
K4[Pt2(pop)4Cl2]2H2O serves only as a bridging 
liggend between two symmetry-related K(2) atoms.

It is of interest to compare the crystal structures of the series 
of binuclear platinum diphosphite complexes K4[Pt2-
and K4[Pt2(pop)CH3I]2H2O. In the first two complexes 
(same space group, P4/mmbm), the roughly cylindrical Pt2-
(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 P1. In K4[Pt2(pop)CH3I]2H2O, the nonin-
teracting Pt2(pop)4 barrels are arranged in columns along 
the c direction, with a much increased interbarrel gap necessitated 
space group P1. It is noteworthy that the a axis of 
K4[Pt2(pop)CH3I]2H2O is approximately equal to half of 
the face diagonal of the base unit cell in either K4-
[Pt2(pop)2]2H2O or K4[Pt2(pop)Br]2H2O (see Figure 1) of 
K4[Pt2(pop)Cl2]2H2O indicating very similar lateral packing of the columns 
in the three tetragonal crystalline compounds.

Acknowledgment. C.-M.C. thanks the Committee on Re-
search and Conference Grants of the University of Hong Kong for 
support. Research at Caltech was supported by National 
Science Foundation Grant CHE81-20419.

Registry No. K4[Pt2(pop)4CH3I]2H2O, 93134-17-9; K4[Pt2(pop)4], 82115-51-1; CH3I, 74-88-4; K4[Pt2(pop)4Cl2]I4, 82135-52-2; Pt, 7440-06-4.

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.

(24) Symmetry-generated O(1) positions at (x, y, z), (x, y, -z), (x, -y, z), (x, -y, -z), (y, x, -z), (y, -x, z), (z, x, -y), (-z, x, y), 
and with O(2) at (x, 0, 0) and 0, 0, 0 with Ow at 2.837 (14) Å.24 Unlike the water molecule in K4[Pt2(pop)4C12]2H2O,10 which is 
hydrogen bonded to diphosphite ions, the 2-fold disordered 
Ow atom in K4[Pt2(pop)4CH3I]2H2O serves only as a bridging 
ligand between two symmetry-related K(2) atoms.

Table II. Atomic Coordinates (×104 for Pt, I, and P; ×104 for K, O, and C) and Equivalent Isotropic Temperature Factors (Å2 × 104 for Pt, I, and P; Å2 × 104 for K, O, and C)

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff position</th>
<th>Site symmetry</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Ueq</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>4(e)</td>
<td>4mm</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>8811 (4)</td>
</tr>
<tr>
<td>I</td>
<td>4(e)</td>
<td>4mm</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>26647 (16)</td>
</tr>
<tr>
<td>P</td>
<td>16(m)</td>
<td>m</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>24670 (19)</td>
</tr>
<tr>
<td>O(1)</td>
<td>32(o)</td>
<td>1</td>
<td>1297 (4)</td>
<td>3138 (5)</td>
<td>1345 (4)</td>
<td>50 (2)</td>
</tr>
<tr>
<td>O(2)</td>
<td>8(i)</td>
<td>mm</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2260 (24)</td>
</tr>
<tr>
<td>K(1)</td>
<td>4(d)</td>
<td>4mm</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>250 (1)</td>
</tr>
<tr>
<td>K(2)</td>
<td>8(j)</td>
<td>mm</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>42 (2)</td>
</tr>
<tr>
<td>Ow</td>
<td>8(j)</td>
<td>mm</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2310 (23)</td>
</tr>
</tbody>
</table>

a Calculated as one-third of the trace of the orthogonalized Ueq matrix. b Symmetry-generated. c Varied isotropically.

Contributed by the Department of Chemistry, 
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6Cu NMR Studies of Copper(I) Complexes. Relationship between 
6Cu Chemical Shift and Metal–Ligand Binding

Susumu Kitagawa* and Megumu Munakata

Received January 5, 1984

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


cu

Inorg. Chem. 1984, 23, 4388–4390
Copper(I) complexes were prepared at 25 °C under a highly purified atmosphere. The metal nuclei, leading to the satisfactory receptivity of its resonance frequency is relatively high among the observable metal nuclei, providing a relatively sharp 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 63Cu 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 (CuL₄) 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, which is also reproduced in acetone solutions containing a low concentration of ligand (([RNC]/[Cu]) = 200).

### 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 quadrupolar relaxation rate. 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 63Cu 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 (CuL₄) completely. The observed chemical shift and line width at half-height are presented in Table I.

### Experimental Section

#### Materials

[Cu(CH₃CN)₂]ClO₄ was utilized as a starting copper(I) source. Isocyanides have been synthesized according to the literature. Pyridines were commercially available and purified before use.

#### Preparation of Copper Complexes

The tetrahedral binary copper(I) complexes suffice for the primary purpose of gaining the correlation of the metal–ligand bonding with 63Cu chemical shift. The large excess concentration of ligand, usually as a solvent, is utilized in order to form the four-coordination copper(I) complex (CuL₄) 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, which is also reproduced in acetone solutions containing a low concentration of ligand (([RNC]/[Cu]) = 200).

### Table I. Observed 63Cu NMR Shifts of [CuL₄]ClO₄

<table>
<thead>
<tr>
<th>L</th>
<th>solvent</th>
<th>Δδ_prel.</th>
<th>Δω line width, Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃CN</td>
<td>CH₃CN</td>
<td>0</td>
<td>500</td>
</tr>
<tr>
<td>C₅H₅CN</td>
<td>C₅H₅CN</td>
<td>13</td>
<td>950</td>
</tr>
<tr>
<td>4-CH₃py</td>
<td>4-CH₃py</td>
<td>108</td>
<td>2830</td>
</tr>
<tr>
<td>3-CH₃py</td>
<td>3-CH₃py</td>
<td>110</td>
<td>1100</td>
</tr>
<tr>
<td>py</td>
<td>H₂O</td>
<td>994</td>
<td>940</td>
</tr>
<tr>
<td>C₅H₅NC</td>
<td>C₅H₅NC</td>
<td>451</td>
<td>4000</td>
</tr>
<tr>
<td>C₅H₅NC</td>
<td>C₅H₅NC</td>
<td>468</td>
<td>880</td>
</tr>
<tr>
<td>4-CH₃C₂H₄NC</td>
<td>4-CH₃C₂H₄NC</td>
<td>547</td>
<td>320</td>
</tr>
<tr>
<td>C₅H₅NC</td>
<td>C₅H₅NC</td>
<td>549</td>
<td>300</td>
</tr>
<tr>
<td>4-CIC₆H₄NC</td>
<td>CH₂CN</td>
<td>553</td>
<td>230</td>
</tr>
</tbody>
</table>

*Observed at 25 °C. 1 Referenced against 0.05 M CH₃CN solution of [Cu(CH₃CN)₂]ClO₄. 2 At half-height. 3 [KCN]/[CuCN] = 5. 4 [RNC]/[Cu] = 200.
The apparent increase antiparallels the increase of the ligand basicity: a) 4-Me-py, $pK_a = 6.03$; 3-Me-py, $pK_a = 5.68$; py, $pK_a = 5.23$. We have demonstrated previously that ligands having good $\pi$-acceptor capability cause the metal to ligand charge-transfer (MLCT) band, L$\rightarrow$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 $\pi$-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 $\pi$-acceptor properties of the pyridine nitrogen.

Second, the substituent effect on $\Delta\delta$ is estimated for copper(I) complexes of isocyanides as well as cyanide ion. The $^{63}$Cu NMR spectra of [Cu(RCN)$_4$]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 $^{13}$C$_N$ is greater than that for the alkyl isocyanide, which is accounted for by the $\pi$-acceptor properties because the $\pi$-acceptor capability of aryl isocyanide is superior to that of alkyl isocyanide. 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 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 C$_2$H$_5$, the other hand, nitrile complexes of copper(I), Cu(RCN)$_4$ (R = Me-py and py), give single sharp lines with quite a large downfield shift ranging 7744–797 ppm. [Cu(C$_6$H$_5$NC)$_4$]ClO$_4$, 93110-85-1; [Cu(CH$_3$NC)$_4$]ClO$_4$, 93110-87-3; [Cu(4-MeC$_6$H$_4$NC)$_4$]ClO$_4$, 7744-79-7; [Cu(C$_6$H$_5$NC)$_4$]ClO$_4$, 93110-88-4; [Cu(4-CIC$_6$H$_4$NC)$_4$]ClO$_4$, 93110-89-5; $^{63}$Cu, 1419I-84-5.

Figure 1. $^{63}$Cu NMR spectra at 25 °C of [Cu(CH$_3$CN)$_4$]ClO$_4$ (1), [Cu(C$_6$H$_5$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).

Table I reveals that propionitrile experiences a downfield shift 13 ppm more than that in the case of acetonitrile, indicative of the sensitivity of the $^{63}$Cu shift.

In conclusion, the $^{63}$Cu resonances are deshielded with an increase in $\pi$-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.

Acknowledgement. We appreciate the assistance of H. Konoike, K. Kameda, and Y. Usda. This work is supported in part by grants from the Ministry of Education of Japan.


Detailed Correlations between the Ligand-to-Metal Charge-Transfer (LMCT) Spectra of Copper(I1) and Ruthenium(III) Imidazoles and Imidazolates. Electronic Structures of Carbon-Bound Ruthenium(III) Imidazoles and Imidazolates

Karsten Krogh-Jespersen* and Harvey J. Schugar*

Received December 8, 1983

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(I1) ligand-to-metal charge-transfer (LMCT) absorptions of model Cu(I1) complexes in order to identify and better understand corresponding absorptions in the spectra of Cu(I1) proteins. Our previous studies have employed Cu(I1)-tetrakis (imidazole) systems, and we have been searching for simpler model complexes that correlate the geometric as well as electronic structures of these chromophores. 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(I1)-imidazolates are poorly characterized. Little is known aside from the observation that Cu(I1)-imidazolates exhibit a LMCT absorption in the near-UV region that is not present in the spectra of reference Cu(I1)-imidazolates complexes. Furthermore, the systems studied were polynuclear imidazole-bridged Cu(I1) complexes, and their suitability as spectroscopic models for the imidazole-bridged Cu(I1)/Zn(I1) unit of superoxide dismutase must be suspect.

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