Ni(II) the M–C σ bonds decrease by 0.04 Å while the perpendicular M–ring distance increases by ~0.05 Å. The shorter σ bond to Ni(II) is reasonable in terms of a nuclear charge effect. The longer π bonds, however, suggest that the highest occupied molecular orbital is antibonding or at least nonbonding with respect to the π-arene ligand.[23] It is hoped that additional structural and theoretical studies will lend insight into two important facets: (1) an understanding of the extreme π-arene lability in this series of compounds which are perhaps the most labile yet reported[5] and (2) an understanding of the significant structural differences that exist between the cobalt and nickel analogues with regard to M–arene π-bond lengths and with regard to distortions of the π-arene framework found in the Ni(II) case but not Co(II). Finally, a variety of other π-arene ligands are also under investigation.

Acknowledgment. Support of this work from Research Corp. (L. J. Radonovich) and the National Science Foundation (K. J. Klabunde, Grant No. CHE-7402713) is acknowledged with gratitude. Acknowledgment is also made to the University of North Dakota for a Summer Research Professorship and a generous contribution of computer time.

Registry No. (η^6-$C_6H_5CH_3$)Co(C_6F_5)$_2$, 60528-58-7; (η^6-$C_6H_5CH_3$)Ni(C_6F_5)$_2$, 66197-14-6.

Supplementary Material Available: Listing of the structure factor amplitudes is available (16 pages). Ordering information is given on any current masthead page.

---

[23] A more detailed discussion of the bonding in this system of compounds including additional X-ray data and results of molecular orbital calculations will be forthcoming. Radonovich, L. J.; Albright, T. A.; Koch, F. J., work in preparation.

Contribution No. 6103 from the Division of Chemistry and Chemical Engineering,
California Institute of Technology, Pasadena, California 91125

Crystal and Molecular Structure of a Mixed-Valent Copper(II)–Copper(I)–Macrocyclic Ligand Complex

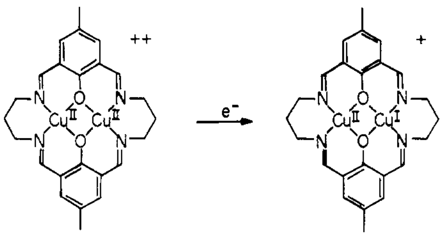
ROBERT R. GAGNÉ,* LAWRENCE M. HENLING, and THOMAS J. KISTENMACHER[1]

Received September 7, 1979

Condensation of 1,3-diaminopropane with 2-hydroxy-5-methylisophthalaldehyde in the presence of copper(II) perchlorate yields the binuclear copper(II)–macrocyclic ligand complex. One-electron electrochemical reduction gives the mixed-valent $Cu^{II}Cu^{I}$ ion **1**, which apparently exhibits facile electron transfer at 298 K. The crystal and molecular structure of **1** reveals distinct copper coordination sites in the solid state. Coordination about Cu1 is square planar with Cu–N bond lengths of 1.98 Å and Cu–O bond lengths of 1.96 Å. The second copper is disordered with 35% in the Cu2a site and 65% in the Cu2b site. The latter, Cu2b, is displaced 0.15 Å from the best plane of two oxygen (Cu2b–O = 2.12 Å) and two nitrogen (Cu2b–N = 1.96 Å) ligands toward an aromatic ring carbon of an adjacent molecule (Cu2b–C = 3.04 Å). More dramatically, Cu2a is displaced 0.65 Å from the two coordinated nitrogens (Cu2a–N = 2.03 Å) and oxygens (Cu2a–O = 2.26 A) toward the same aromatic ring carbon of the adjacent molecule. The overall geometry of Cu2a is square pyramidal with a Cu2a–C distance of 2.55 Å which suggests a favorable interaction. The molecular structure yields no evidence of thermal electron transfer in the solid state, but the possibility of photoassisted electron transfer cannot be precluded. This structure may represent one conformational form of the mixed-valent species in solution. It further suggests that conformational changes may be the limiting factor in the solution intramolecular electron-transfer rate.

Introduction

The synthesis and characterization of the mixed-valent $Cu^{II}Cu^{I}$–macrocyclic ligand complex **1** were recently reported.



1

With two identical Schiff-base ligand coordination sites, it was expected that complex **1** might exhibit facile intramolecular electron transfer. Indeed, the mixed-valent ion, which is stable to disproportionation, exhibits both photoassisted and thermal intramolecular electron transfer, as evidenced by electronic absorption and EPR spectra.[2,3]

Solution EPR spectra are temperature dependent. At the ambient temperature a seven-line spectrum was observed, indicating that the single unpaired electron is interacting with both copper ions. As the solution temperature was lowered, a four-line spectrum was produced, consistent with localization of the electron on a single metal site. From this variable-temperature behavior a value of $1.7 \times 10^{10}\ s^{-1}$ at 298 K was estimated for the thermal intramolecular electron-transfer rate. Unfortunately, solid-state measurements yielded little information since the EPR spectrum of the magnetically nondilute solid consists of only a single line.

Electronic absorption spectra of the mixed-valent species, **1**, are more complex. Several solvent-dependent bands were observed for the complex in the region 600–1700 nm. These absorptions are not present in the precursor $Cu^{II}Cu^{II}$ complex and may be attributable to photoassisted intervalent transfer (eq 1). Mull spectra indicate that similar transitions occur

$$[\mathrm{Cu^{II}Cu^{I}L^{+}}] \xrightarrow{h\nu} [\mathrm{Cu^{I}Cu^{II}L^{+}}]^{*} \qquad (1)$$

---

[1] On sabbatical leave from the Department of Chemistry, The Johns Hopkins University.

[2] Gagné, R. R.; Koval, C. A.; Smith, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 8367.

[3] Gagné, R. R.; Koval, C. A.; Smith, T. J.; Cimolino, M. C. *J. Am. Chem. Soc.* **1979**, *101*, 4571.

Table I. Summary of Crystal Data

formula $Cu_2C_{24}H_{26}N_4O_6Cl\cdot(CH_3OH)_{0.5}$
fw 645.06
space group $P\bar{1}$
$Z = 2$
$\mu = 35.81$ cm^{-1}
$\rho_{calcd} = 1.72$ g/cm^3
ρ_{obsd}(flotation) = 1.70 g/cm^3
λ(Cu Kα) = 1.5418 Å

$a = 11.861$ (2) Å
$b = 8.265$ (2) Å
$c = 14.076$ (3) Å
$\alpha = 104.27$ (2)°
$\beta = 104.68$ (2)°
$\gamma = 100.88$ (2)°
$V = 1246.5$ (10) Å^3

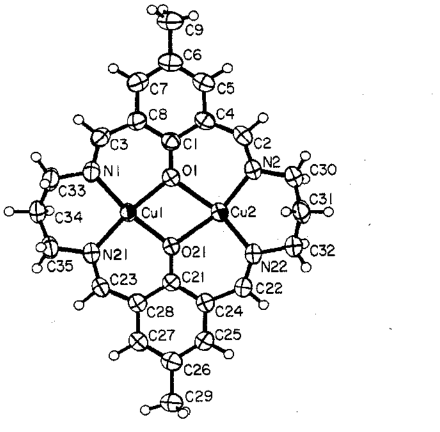


Figure 1. The mixed-valent cation projected onto the best plane through the four nitrogen atoms showing the labeling scheme used. For clarity, the Cu2a and Cu2b sites are represented by a single elongated ellipsoid. All thermal ellipsoids are drawn at the 50% probability level with the exception of the arbitrarily sized hydrogen spheres.

in the solid state, suggesting possible structural similarities between the solution- and solid-state species.

An X-ray structural analysis was undertaken to further elucidate the nature of the mixed-valent complex, **1**. There are two electronic states which are consistent with the ambient-temperature spectral results and which may be structurally distinguishable. The single unpaired electron may be delocalized over both copper sites, in which case the complex is best described as containing Cu$^{1.5}$Cu$^{1.5}$ and no intervalence transfer takes place. Such a species would be expected to have structurally identical copper sites. Alternatively, the electron may be localized on one copper ion and the valence trapped as Cu^{II}Cu^{I} with rapid electron transfer between the two copper ions. Structurally, the two copper sites would be nonequivalent, but the differences could be small and the sites indistinguishable. For example, the crystal structure of the mixed-valent μ-pyrazine-bis(pentaammineruthenium)(5+) ion failed to distinguish the two ruthenium sites.[4] We report here that the Cu^{II}Cu^{I} complex, **1**, contains distinct copper coordination sites in the solid state.

Results

Crystal data for the binuclear complex are summarized in Table I. An atomic numbering scheme is shown in Figure 1; atomic parameters, bond lengths, and bond angles are presented in Tables II–IV and Figure 2. The space group is $P\bar{1}$ with two complex cations (Figure 1), two perchlorate anions, and one disordered methanol molecule in the unit cell (Figure 3). Within the crystal, the flat cations are all parallel and are arranged in slipped stacks, with two alternating kinds of overlap (Figure 4). The intermolecular distance, measured between the best planes through the four nitrogen atoms, is 3.37 Å in both cases.

The binuclear cation is essentially planar. The two four-coordinate copper atoms, Cu1 and Cu2, are each bonded to two imine nitrogen atoms and share the two bridging phenolate oxygens. The coordination about Cu1 is square planar; the copper ion lies in the best plane of the four ligating atoms. The two copper–nitrogen bonds average 1.98 Å; the copper–oxygen bonds average 1.96 Å. Directly above Cu1 at a distance of 3.43 Å is a symmetry-related copper atom in another cation (Figure 4). The nearest atom on the other side is an aromatic carbon, C4, in the cation below. This carbon is 3.40 Å away and is not directly beneath the copper.

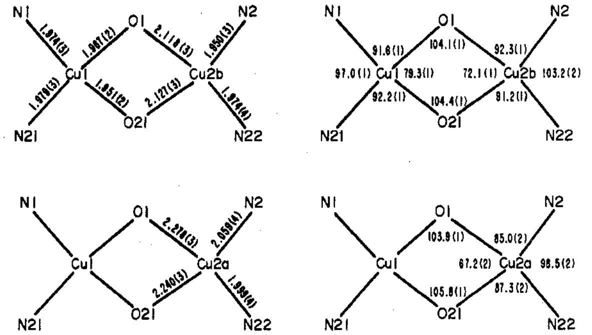


Figure 2. Coordination-sphere bond lengths (Å) and angles (deg) for the three types of copper atoms, Cu1, Cu2a, and Cu2b, used in the structure refinement. Numbers in parentheses are estimated standard deviations in units of the last digit.

The second copper atom is disordered over two sites either statically or dynamically, although the four coordinated ligand atoms are not noticeably disordered. The two sites, Cu2a and Cu2b, which are 0.51 Å apart, have populations of 35% and 65%, respectively. The copper coordination of the more populated position, Cu2b, is only approximately square planar. The copper atom is displaced 0.15 Å from the best plane through its two oxygen and two nitrogen ligands toward an aromatic carbon, C8, of an adjacent cation (Figures 1 and 4). The Cu2b to C8 distance is 3.04 Å. On the opposite side of Cu2b is a bent-away trimethylene bridge. The average Cu2b–N bond length is 1.96 Å, close to that for Cu1. Substantially longer, however, is the average Cu2b–O bond length at 2.12 Å.

The last copper site, Cu2a, might be best described as square pyramidal. It is displaced, in the same direction as Cu2b, 0.65 Å from the basal plane comprised of O1, O21, N2, and N22. In this position it is only 2.55 Å from the aromatic carbon, C8, in an adjacent molecule, well within the sum of the van der Waals radii, which is 3.1 Å. This apparently favorable interaction produces no significant perturbation in either the geometry or thermal parameters of C8 when compared with those of chemically similar atoms C4, C28, and C24. The next two shortest Cu–C distances are to C7, at 2.83 Å, and C3, at 2.95 Å. The Cu2a–N and Cu2a–O bonds are the longest observed in this complex, averaging 2.03 and 2.26 Å, respectively.

The macrocyclic ligand is in an overall chair conformation, with the central carbons of the trimethylene bridges bent, in opposite directions, ~0.7 Å farther out of the best plane for the four nitrogen atoms than the adjacent carbon atoms. Additionally, the out-of-the-plane copper, Cu2, its coordinated imine nitrogens, N2 and N22, and the adjacent three methylene carbons, C30, C31, and C32, are also in a chair conformation. The remainder of the macrocyclic ligand is slightly buckled (Figure 4) due partly to a minor twisting and bending back of the two phenyl rings from the best plane of the four nitrogen atoms (Table V).

Lying in the parallel sheets formed by the cations are the perchlorate anions and the poorly resolved solvent molecules. The perchlorate ion geometry is normal, with bond lengths ranging from 1.38 to 1.40 Å and bond angles from 105.9 to 113.7°. The disordered methanol molecules may be weakly

---

(4) Beattie, J. K.; Hush, N. S.; Taylor, P. R.; Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1977**, 1121.

Table II. Final Parameters for $Cu^{I}Cu^{II}L(ClO_4)$[a]

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu1	4 959 (5)	32 646 (7)	44 961 (4)	369 (3)	420 (3)	456 (3)	58 (2)	143 (2)	124 (2)
O1	−4 794 (22)	17 924 (34)	50 629 (18)	427 (14)	511 (16)	432 (13)	53 (12)	140 (11)	168 (12)
O21	−9 716 (21)	21 890 (33)	33 145 (18)	388 (13)	487 (15)	453 (13)	34 (11)	124 (11)	176 (12)
N1	18 228 (27)	42 001 (43)	58 213 (25)	393 (16)	493 (19)	525 (18)	47 (14)	140 (13)	122 (15)
N2	−28 400 (28)	−5 840 (44)	46 749 (25)	470 (18)	523 (20)	540 (18)	36 (15)	185 (15)	184 (16)
N21	12 911 (27)	45 435 (42)	37 195 (24)	410 (16)	464 (19)	552 (19)	55 (14)	146 (14)	152 (15)
N22	−34 152 (28)	−1 710 (47)	25 052 (26)	421 (17)	626 (22)	554 (19)	17 (16)	121 (14)	212 (17)
C1	−2 424 (33)	16 177 (48)	59 900 (27)	475 (20)	441 (21)	437 (18)	125 (17)	169 (15)	141 (16)
C21	−12 454 (31)	24 170 (49)	23 961 (26)	414 (18)	471 (21)	417 (18)	107 (16)	137 (14)	136 (16)
C2	−23 532 (36)	−3 344 (51)	56 490 (30)	580 (23)	443 (22)	566 (22)	122 (18)	294 (19)	194 (18)
C22	−34 207 (34)	4 921 (59)	17 750 (31)	420 (20)	689 (28)	539 (22)	27 (19)	98 (17)	222 (21)
C3	18 213 (35)	36 769 (55)	66 188 (29)	471 (21)	572 (25)	444 (19)	124 (18)	86 (16)	96 (18)
C23	7 883 (34)	44 386 (53)	27 780 (30)	451 (20)	536 (24)	573 (23)	59 (18)	206 (17)	234 (19)
C4	−11 250 (36)	5 951 (51)	62 880 (29)	555 (22)	473 (22)	508 (20)	169 (18)	263 (17)	188 (17)
C5	−8 329 (39)	4 851 (54)	72 966 (29)	680 (26)	527 (24)	494 (21)	184 (20)	282 (19)	207 (19)
C6	2 887 (43)	12 989 (58)	80 348 (31)	781 (30)	602 (27)	479 (21)	279 (23)	249 (20)	195 (20)
C7	11 332 (38)	22 677 (58)	17 486 (29)	586 (24)	619 (27)	443 (20)	151 (21)	117 (18)	162 (19)
C8	8 974 (36)	24 495 (54)	81 476 (29)	518 (22)	534 (24)	465 (20)	134 (18)	150 (17)	121 (18)
C9	5 585 (49)	11 599 (71)	91 173 (33)	929 (35)	848 (36)	465 (23)	236 (29)	209 (23)	253 (24)
C24	−24 149 (34)	16 292 (54)	16 497 (29)	435 (20)	578 (25)	499 (20)	63 (17)	146 (16)	204 (19)
C25	−26 678 (36)	19 262 (62)	6 919 (31)	465 (22)	757 (30)	516 (22)	55 (21)	93 (17)	238 (22)
C26	−18 417 (41)	29 511 (65)	4 066 (32)	612 (26)	798 (32)	521 (23)	130 (23)	192 (20)	296 (23)
C27	−7 128 (37)	37 271 (59)	11 300 (31)	541 (24)	688 (28)	557 (23)	64 (21)	216 (19)	288 (22)
C28	−4 071 (33)	34 836 (51)	21 142 (28)	458 (20)	489 (22)	485 (20)	88 (17)	175 (16)	162 (17)
C29	−21 460 (46)	32 328 (86)	−6 469 (38)	670 (30)	1345 (53)	626 (29)	44 (32)	132 (24)	520 (33)
C30	−41 145 (38)	−16 046 (59)	42 219 (33)	539 (24)	617 (27)	631 (25)	0 (20)	220 (20)	233 (22)
C31	−48 409 (36)	−9 332 (62)	34 422 (38)	437 (22)	670 (29)	861 (32)	81 (20)	237 (21)	322 (26)
C32	−45 695 (39)	−12 944 (69)	24 286 (36)	501 (24)	840 (34)	649 (27)	−81 (23)	104 (20)	277 (26)
C33	28 995 (36)	55 736 (59)	59 675 (33)	441 (21)	609 (27)	628 (25)	−54 (19)	123 (19)	72 (21)
C34	33 187 (33)	53 182 (55)	50 391 (33)	388 (20)	542 (24)	673 (25)	29 (17)	162 (18)	169 (21)
C35	25 236 (37)	57 583 (59)	41 767 (36)	481 (22)	569 (26)	763 (28)	−5 (19)	157 (20)	271 (23)
Cl	36 571 (10)	28 041 (16)	20 481 (9)	574 (7)	664 (8)	616 (6)	120 (6)	161 (5)	233 (6)
O3	24 359 (45)	25 175 (107)	16 372 (46)	897 (34)	3044 (91)	1434 (45)	551 (47)	15 (33)	667 (56)
O4	39 177 (48)	23 474 (87)	29 591 (40)	1416 (42)	2280 (67)	1305 (40)	510 (43)	322 (34)	1269 (46)
O5	41 782 (71)	20 330 (102)	13 719 (50)	2932 (87)	2408 (82)	1830 (62)	1613 (72)	1639 (67)	816 (59)
O6	41 489 (66)	45 660 (70)	23 402 (52)	2603 (79)	813 (36)	1928 (62)	−165 (43)	673 (59)	399 (40)

	x	y	z	B, Å^2	population		x	y	z	B, Å^2	population
Cu2a	−1973 (2)	−85 (5)	3641 (2)	3.35 (0.06)	0.347 (7)	CM	5090	5000	70	10.00	0.5
Cu2b	−2081 (1)	456 (3)	3812 (1)	3.59 (0.03)	0.653 (7)	O1M	5880	5120	960	9.50	0.25
						O2M	4130	3600	−379	10.50	0.25

[a] The fractional coordinates of the anisotropic atoms are multiplied by 10^5, those of the other atoms by 10^4. The form of the temperature factor is $\exp(-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{23}klb^*c^*))$. The U_{ij} are multiplied by 10^4. Numbers in parentheses are estimated standard deviations in units of the last digit.

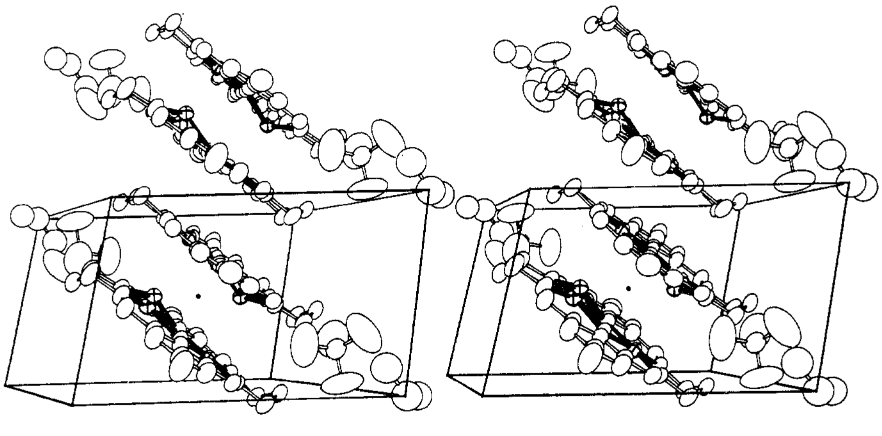


Figure 3. A stereoview of the crystal structure with thermal ellipsoids drawn at the 50% level. The crystallographic center of symmetry at 0, 0, 0 is represented by a dot. The outline of the unit cell has been translated by $-^1/_2$, $-^1/_2$, $-^1/_2$. Two of the disordered methanol oxygens, related by a center of symmetry to the two shown, have not been drawn.

hydrogen bonded to the perchlorate ion. There do not appear to be any strong interactions between the cations and the anions or solvent molecules.

Discussion

In the solid state complex **1** can probably best be described in terms of localized valence states, with one divalent copper ion (Cu1) and two types of monovalent copper ions (Cu2a and Cu2b). In contrast, the crystal and molecular structure of an unreduced analogue, $Cu^{II}Cu^{II}LCl_2 \cdot 6H_2O$, revealed two identical copper sites.[5] In the latter complex the chlorides are coordinated, resulting in square-pyramidal geometry about the

---

(5) Hoskins, B. F.; McLeod, N. J.; Schaap, H. A. *Aust. J. Chem.* **1976**, *29*, 515.

Table III. Interatomic Distances (Å)[a]

	Intramolecular Distances		
O1-C1	1.314 (4)	C3-N1	1.299 (5)
C1-C4	1.432 (5)	N1-C33	1.472 (5)
C1-C8	1.412 (5)	C33-C34	1.494 (6)
C4-C5	1.404 (6)	C34-C35	1.504 (6)
C5-C6	1.385 (6)	C35-N21	1.487 (5)
C6-C9	1.513 (7)	N21-C23	1.282 (5)
C6-C7	1.368 (6)	C23-C28	1.432 (5)
C7-C8	1.414 (6)	C28-C27	1.415 (6)
C8-C3	1.426 (6)		
C27-C26	1.380 (6)	C32-C31	1.512 (7)
C26-C29	1.521 (7)	C31-C30	1.502 (6)
C26-C25	1.376 (6)	C30-N2	1.473 (5)
C25-C24	1.398 (6)	N2-C2	1.292 (5)
C24-C21	1.427 (5)	C2-C4	1.447 (5)
C21-O21	1.320 (4)	Cu1-Cu2a	3.348 (3)
C24-C22	1.450 (6)	Cu1-Cu2b	3.223 (1)
C22-N22	1.278 (5)	Cu2a-Cu2b	0.510 (3)
N22-C32	1.464 (6)		
	Intermolecular Distances		
Cu1-Cu1[b]	3.426 (1)	Cu2a-C3[c]	2.945 (5)
Cu2a-C8[c]	2.552 (5)	Cu2b-C8[c]	3.044 (4)
Cu2a-C7[c]	2.826 (5)		

[a] See also Figure 2. Numbers in parentheses are estimated standard deviations in units of the last digit. [b] Coordinates related by $-x, 1-y, 1-z$. [c] Coordinates related by $-x, -y, 1-z$.

Table IV. Bond Angles (Deg)[a]

N21-Cu1-O1	171.3 (1)	N21-C23-C28	128.6 (4)
N1-Cu1-O21	170.6 (1)	C23-C28-C21	124.4 (4)
O1-Cu2a-N22	141.9 (2)	C23-C28-C27	114.6 (4)
O21-Cu2a-N2	139.1 (2)	C21-C28-C27	121.0 (4)
O1-Cu2b-N22	162.3 (2)	C28-C27-C26	122.3 (4)
O21-Cu2b-N2	162.3 (2)	C27-C26-C29	121.2 (4)
Cu2a-O1-C1	124.5 (2)	C29-C26-C25	122.3 (5)
Cu2b-O1-C1	125.6 (2)	C27-C26-C25	116.5 (4)
Cu1-O1-C1	130.3 (2)	C26-C25-C24	123.7 (4)
O1-C1-C8	121.4 (4)	C25-C24-C22	114.0 (4)
O1-C1-C4	121.9 (4)	C25-C24-C21	119.9 (4)
C8-C1-C4	116.7 (4)	C21-C24-C22	126.1 (4)
C1-C4-C5	119.6 (4)	C28-C21-O21	121.5 (3)
C1-C4-C2	126.1 (4)	C28-C21-C24	116.5 (4)
C5-C4-C2	114.3 (4)	C24-C21-O21	121.9 (3)
C4-C5-C6	123.5 (4)	C21-O21-Cu1	129.6 (2)
C5-C6-C9	121.6 (4)	C21-O21-Cu2a	122.9 (2)
C5-C6-C7	116.9 (4)	C21-O21-Cu2b	126.0 (2)
C9-C6-C7	121.5 (4)	C24-C22-N22	127.9 (4)
C6-C7-C8	122.7 (4)	C22-N22-C32	116.2 (4)
C7-C8-C1	120.7 (4)	C22-N22-Cu2a	127.1 (3)
C7-C8-C3	115.2 (4)	C22-N22-Cu2b	126.0 (3)
C3-C8-C1	123.6 (4)	Cu2a-N22-C32	116.2 (3)
C8-C3-N1	129.0 (4)	Cu2b-N22-C32	117.1 (3)
C3-N1-Cu1	123.7 (3)	N22-C32-C31	112.6 (4)
C3-N1-C33	115.2 (4)	C32-C31-C30	114.3 (4)
C33-N1-Cu1	121.1 (3)	C31-C30-N2	112.7 (4)
N1-C33-C34	112.6 (4)	C30-N2-C2	116.0 (4)
C33-C34-C35	112.6 (4)	C30-N2-Cu2a	115.8 (3)
C34-C35-N21	112.9 (4)	C30-N2-Cu2b	118.3 (3)
C35-N21-Cu1	123.4 (3)	Cu2a-N2-C2	127.3 (3)
C35-N21-C23	113.0 (4)	Cu2b-N2-C2	125.5 (3)
Cu1-N21-C23	123.6 (3)	N2-C2-C4	127.9 (4)

[a] See also Figure 2. Numbers in parentheses are estimated standard deviations in units of the last digit.

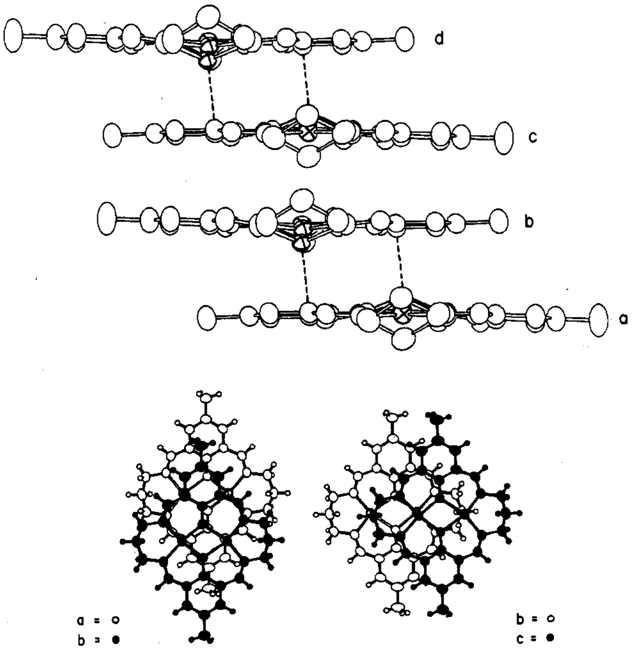


Figure 4. Stacking interactions of the cations. The four cations a, b, c, and d are related by the following symmetry transforms: (a) $-x, -y, 1-z$; (b) x, y, z; (c) $-x, 1-y, 1-z$; (d) $x, 1+y, z$. The upper figure is a projection perpendicular to the best plane through the four nitrogens with the methyl carbons extending on either side. It illustrates the three types of copper atoms, Cu1, Cu2a, and Cu2b, the Cu2a–carbon interaction (dotted lines), and the minor deformation of the macrocyclic ligand. In this figure only Cu1 is visible in cations a and c; in cations b and d, Cu2a projects down from the macrocyclic plane, directly beneath Cu2b, which obscures most of Cu1. The lower figures show the two types of overlap present. In cation b, Cu1 lies on the left and Cu2 (again one ellipsoid) on the right; in cations a and c the order is reversed.

Table V. Best Plane through the Four Nitrogen Atoms

atom	dev, Å	atom	dev, Å
Cu1	−0.0234	C4	−0.0166
Cu2a	−0.6677	C5	0.0064
Cu2b	−0.1656	C6	−0.0668
C1	−0.0955	C7	−0.1498
C21	0.0679	C8	−0.1644
C2	0.0914	C9	−0.0229
C22	0.2335	C24	0.1925
C3	−0.0832	C25	0.2815
C23	−0.0006		
C26	0.2513	C31	0.8851
C27	0.1423	C32	0.1138
C28	0.0574	C33	0.1651
C29	0.3389	C34	−0.6207
C30	0.1266	C35	0.0082
O1	−0.0911	N2	−0.0144
O2	−0.0032	N21	−0.0149
N1	0.0149	N22	0.0144

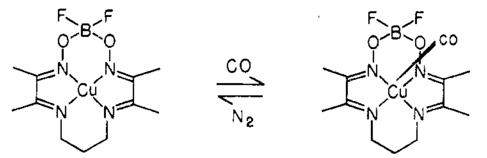
copper ions, each of which is displaced 0.21 Å from its basal plane. The Cu–N and Cu–O bond lengths of 1.98 Å in $Cu^{II}Cu^{II}LCl_2{\cdot}6H_2O$ agree well with those observed in the Cu1 site in the mixed-valent compound, reported herein.

While Cu1 appears to be a typical divalent copper ion, the geometry about Cu2 is not the tetrahedron favored for four-coordinate monovalent copper complexes. The rigid near-planar nature of the macrocyclic ligand may prevent the distortion required for the tetrahedral coordination. The observed geometry about Cu2a and Cu2b might be accounted for by comparison with other known Cu(I) complexes. In addition to coordinating two nitrogen and two oxygen ligands, the Cu2a ion projects into part of the π system of an adjacent macrocycle. This weak attraction may be similar to that between Cu(I) and CO in a recently reported five-coordinate Cu(I) complex. In the four-coordinate Cu(I)–macrocyclic ligand complex **2** the copper atom lies in the best plane through the four nitrogens, although the ligand is tetrahedrally distorted.[6] The average Cu–N bond length is 1.94 Å, which

---

(6) Gagné, R. R.; Allison, J. L.; Lisensky, G. C. *Inorg. Chem.* **1978**, *17*, 3563.

lengthens to 2.13 Å in the five-coordinate Cu(LBF$_2$)CO, **3**.



2 **3**

In the carbonyl adduct the copper is displaced 0.96 Å from the basal plane and achieves a Cu–C distance of 1.78 Å.[7] This system provides an extreme example with which to compare the mixed-valent ion, **1**, for in the latter case there is certainly not as strong a Cu–C bond as in Cu(LBF$_2$)CO, **3**. Nevertheless, the Cu(LBF$_2$), **2**, and Cu(LBF$_2$)CO, **3**, structures suggest the result of constraining a Cu(I) to a square-planar geometry; the metal atom apparently favors a more spherical arrangement of ligands to the extent that it will form a 20-electron adduct to achieve a more desirable geometry. The copper(I) ion in the mixed-valent species, Cu2, exists in two energetically similar conformations. The Cu2b site is essentially square planar, but in the Cu2a site an added axial interaction with the aromatic ring stabilizes the out-of-plane position of the copper. This displacement may also be attributable, in part, to the constrained macrocyclic hole size and the expected relatively long bonds between soft copper(I) and the hard phenolate oxygens. Indeed, the only similar, structurally characterized complex has a Cu(I)–O bond length of 2.1 Å.[8] That Cu2 is either statically or dynamically disordered may be attributable to relatively weak interactions between Cu(I) and the hard phenolate oxygens and the aromatic π system.[9]

Relating the solid-state structure reported here to possible solution structures is difficult. Solution intramolecular electron transfer results in exchange of valence and, most likely, coordination geometry between the two copper ions in the binuclear complex. There is no evidence of solution intermolecular interactions, and the flexible solvent sphere should permit facile geometry rearrangement to accompany valence changes. In the crystalline lattice, however, the ion lies in a rigid asymmetric environment. Thus one orientation (Cu^{I}Cu^{II} vs. Cu^{II}Cu^{I}) is expected to be more favorable energetically due to the difference in intramolecular interactions for the two arrangements. These intermolecular solid-state forces are apparently sufficiently strong that only one of the two orientations is observed; viz., the Cu(II) is localized as the Cu1 site.

The structure of the Cu^{II}Cu^{I} complex, **1**, suggests that there is no facile thermal intramolecular electron transfer in the solid state. It should be noted, however, that complex **1** exhibits similar electronic absorption spectra in solution and in the solid state, suggesting that photoassisted electron transfer may occur in both states. Indeed, the structure reported here may represent one conformation of the solution species. That solution thermal intramolecular electron transfer in **1** is relatively slow (1.7×10^{10} s^{-1} at 298 K)[3] may be due to large conformational changes as suggested by this structure, which must accompany electron transfer.

It is clearly desirable to obtain additional structural information on mixed-valent complexes in order to establish relationships between structure and intramolecular electron-transfer properties. Derivatives of macrocyclic ligands such as in **1** may prove especially helpful.

Experimental Section

Preparation of Cu^{II}Cu^{I}L(ClO$_4$)·0.5CH$_3$OH. The binuclear Cu^{II}Cu^{II}L(ClO$_4$)$_2$·2H$_2$O was prepared by the method of Pilkington and Robson.[10] The mixed-valent complex Cu^{II}Cu^{I}L(ClO$_4$)·0.5CH$_3$OH was obtained electrochemically by the reported procedure.[3] Cooling of a hot solution of the product in methanol gave dark brown needles. Quantitative gas chromatographic analysis with pyridine as solvent and *o*-xylene as an internal standard confirmed 85% of the methanol expected.

X-ray Data Collection. The crystals were cut to an appropriate length for data collection with a razor blade. Preliminary Weissenberg and precession photographs indicated that the structure possessed triclinic symmetry. Diffraction intensities were collected on an automated full-circle diffractometer using nickel-filtered Cu Kα radiation. Because the material, at least in very small needles or fragments, oxidizes slowly in the atmosphere, the crystals used for data collection were protected with a thin coating of GE No. 7031 varnish. Intensities were recorded by using the θ–2θ scan technique with a scan rate of 1°/min. The scan range was extended 1° on either side of the calculated Kα_1 and Kα_2 peak positions with a stationary-background count for half the scan time at each extreme. Data were collected for $2\theta \leq 158°$ by utilizing both parallel and bisecting modes. Three check reflections measured periodically showed a continuous decline in intensity. When the initial values had decreased by 10%, about halfway through the data collection, the crystal was replaced. The remaining reflections were recorded by using a second crystal. The first crystal was approximately $0.08 \times 0.23 \times 0.40$ mm; the second $0.08 \times 0.15 \times 0.46$ mm.

A total of 5175 unique reflections was obtained. Unit cell constants were determined by averaging 11 sets (5 from the first crystal, 6 from the second) of least-squares fits to 15 centered reflections measured during the course of data collection.

Structure Solution and Refinement. Literature values were used for the neutral atom scattering factors for H,[11] C,[12] N,[12] O,[12] Cu,[13] and Cl.[13] For both Cu and Cl the real component of anomalous dispersion[14] was taken into account. The data sets for the two crystals were merged by using a scale factor calculated from 267 reflections common to both data sets. The combined data were corrected for Lorentz and polarization effects but not for absorption ($\mu = 35.81$ cm^{-1}). Standard deviations of intensities were calculated by using the formula

$$\sigma^2(I) = S + (B_1 + B_2) + (dS)^2$$

where S, B_1, and B_2 are the scan and two background counts and d was taken as 0.02.[15] The largest reflection, ($\bar{2}21$), was too intense to measure accurately and was given zero weight. Two other reflections, ($00\bar{1}$) and ($10\bar{1}$), were given reduced weights for the same reason. The zero-moment test of Howells, Phillips, and Rogers indicated that the crystal structure was centrosymmetric, or $P\bar{1}$.[16,17] The function minimized in the least-squares refinement was $\sum w(|F_o|^2 - |k'F_c|^2)^2$ with the weight w equal to $\sigma^{-2}(F_o^2)$, where F_o and F_c are the observed and calculated structure factors and k' is the inverse of the scale factor k for F_o. The R index is $\sum||F_o| - |F_c||/\sum|F_o|$.[19]

Most of the atoms in the asymmetric unit were found by direct methods.[21] Subsequent difference Fourier maps on a restricted data

---

(7) Gagné, R. R.; Allison, J. L.; Gall, R. S.; Koval, C. A. *J. Am. Chem. Soc.* **1977**, *99*, 7170.

(8) Gagné, R. R.; Kreh, R. P.; Dodge, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 6917.

(9) Another possibility invokes a mixture of two materials, such as Cu^{II}Cu^{I} mixed with Cu^{II}Cu^{II}. This is unlikely since, for example, only a stoichiometric amount of the anion, perchlorate, was located.

(10) Pilkington, N. H.; Robson, R. *Aust. J. Chem.* **1970**, *23*, 2225.

(11) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(12) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1962; Vol. III.

(13) Thomas, L. H.; Umeda, K. *J. Chem. Phys.* **1957**, *26*, 293.

(14) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(15) Peterson, S. W.; Levy, H. A. *Acta Crystallogr.* **1957**, *10*, 70.

(16) Howells, E. R.; Phillips, D. C.; Rogers, D. *Acta Crystallogr.* **1950**, *3*, 210.

(17) The space group $P1$ (replacement of the disordered molecules with two closely related molecules) is not consistent with the populations obtained for the disordered copper atom, 35% and 65% for the two sites. Matrix singularities should also preclude refinement in this space group.[18]

(18) Marsh, R. E.; Schomaker, V. *Inorg. Chem.* **1979**, *18*, 2331.

(19) Except for ORTEP[20] and MULTAN,[21] all computer programs used were from the CRYM crystallographic computing system.

(20) Johnson, C. K. "ORTEP, a Fortran Thermal Ellipsoid Plot Program", Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, Tenn., 1965.

set yielded the positions of the remaining nonhydrogen atoms. A difference map computed after full-matrix isotropic refinement showed electron density in a region where no atoms were expected. This was interpreted as a disordered methanol molecule and fitted isotropically with one oxygen and two disordered carbon atoms. Several cycles of blocked least-squares refinement were then undertaken in which the atomic coordinates were refined in one matrix and the anisotropic temperature factors and the scale factor in another. The methanol parameters were not refined. A subsequent difference map then revealed the six methyl hydrogens. The other hydrogen atom positions were calculated by using a C–H bond length of 1.0 Å; all positions showed appreciable electron density. The hydrogen atoms were given isotropic temperature factors 1.0 Å^2 larger than the isotropic temperature factors of the atoms to which they were bonded. The final refinement of the 334 parameters, not including the parameters for the methanol or hydrogen atoms, was performed with the same two matrices by using all 4703 reflections with $I > \sigma(I)$. The final R index was 0.066. The only features above 0.7 e/Å^3 on a late difference map were near the copper atoms.

In the above model, one of the two copper atoms (Cu2) exhibited an unusually elongated thermal ellipsoid. A difference Fourier map in the plane of the two largest principal axes suggested disorder; several more cycles of refinement were run in which the anisotropic copper was replaced by two isotropic copper atoms and a population factor. This second model has the same number of parameters as the first. It converged as well to an R of 0.065. The final goodness of fit, $\sum w(k^2F_o^2 - F_c^2)^2/(n-p)$, where n is the number of observations and p the number of parameters, was 1.48. Another difference map in the same plane indicated that this model was indeed slightly better in representing the observed electron density. A final difference Fourier map of the entire asymmetric unit was essentially featureless.

Acknowledgment. We gratefully appreciate assistance from T. J. Smith and financial assistance from the National Science Foundation (Grant No. CHE 76-82124).

Registry No. Cu^{II}Cu^{I}L(ClO$_4$)·0.5CH$_3$OH, 72882-14-5.

Supplementary Material Available: Listings of observed and calculated structure factors and hydrogen atom parameters (30 pages). Ordering information is given on any current masthead page.

---

(21) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *27*, 368. Main, P.; Woolfson, M. M.; Lessinger, L.; Germain, G.; Declerq, J. D. "Multan 74, a System of Computing Programmes for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data"; University of York, York, England, and Laboratoire de Chimie Physique et de Cristallographic, Louvain-la-Neuve, Belgium, Dec 1974.

Contribution from the Department of Chemistry,
Northwestern University, Evanston, Illinois 60201

Structure of Bis(triphenylphosphine)(tetrachlorodiazocyclopentadiene)chloroiridium(I) Toluene Solvate, IrCl(N$_2$C$_5$Cl$_4$)(P(C$_6$H$_5$)$_3$)$_2$·C$_7$H$_8$

K. DAHL SCHRAMM and JAMES A. IBERS*

Received September 27, 1979

The structure of bis(triphenylphosphine)(tetrachlorodiazocyclopentadiene)chloroiridium(I) toluene solvate, IrCl(N$_2$C$_5$Cl$_4$)(PPh$_3$)$_2$·C$_7$H$_8$, has been determined crystallographically and consists of discrete molecules of the neutral diazo complex and solvent. The complex crystallizes from toluene–hexane in the monoclinic space group C_{2h}^5-$P2_1/c$ with four formula units in a unit cell of dimensions a = 12.136 (4) Å, b = 24.276 (15) Å, c = 17.849 (7) Å, β = 121.13 (2)°, ρ_{obsd} = 1.56 (3) g/cm^3, and ρ_{calcd} = 1.584 g/cm^3. The structure was solved by Patterson methods. Least-squares refinement has led to a final value of the conventional R index of 0.048 based on 5704 reflections. This complex of iridium(I) possesses square-planar geometry with trans phosphine ligands, P(1)–Ir–P(2) = 176.46 (7)°; the neutral diazo ligand N$_2$C$_5$Cl$_4$ is trans to Cl(1), Cl(1)–Ir–N(1) = 172.72 (19)°, and possesses the singly bent geometry Ir–N(1)–N(2) = 174.6 (6)° and N(1)–N(2)–C(1) = 141.2 (7)°. The substituted cyclopentadiene ring displays regular planar geometry with average C–C distances of 1.39 (2) Å and angles of 108.1 (16)°. Some important molecular parameters are Ir–N(1) = 1.824 (6) Å, N(1)–N(2) = 1.163 (7) Å, N(2)–C(1) = 1.347 (9) Å, Ir–Cl(1) = 2.297 (2) Å, Ir–P(1) = 2.338 (2) Å, and Ir–P(2) = 2.350 (2) Å.

During the past 10 years, there has been a growing interest in the synthesis and structures of transition-metal compounds containing the aryldiazo ligand, N$_2$R$^+$.[1,2] Aryldiazo complexes have been reported for all the members of the Cr, Mn, Fe, Co, and Ni triads with the exception of Ni and Tc.[3–5] Part of the interest in aryldiazo and other diazo ligands has been generated by their close relationship to dinitrogen and nitrosyl ligands. Aryldiazo ligands, like nitrosyl ligands, have been found to adopt varying modes of attachment to transition metals,[5,6] and such variations may be used as a sensitive probe of the metal center and its reaction chemistry.[7–9] In spite of the fact that

---

(1) Albini, A.; Kisch, H. *Top. Curr. Chem.* **1976**, *65*, 105–45.

(2) Sutton, D. *Chem. Soc. Rev.* **1975**, *4*, 443–70.

(3) Haymore, B. L.; Ibers, J. A.; Meek, D. W. *Inorg. Chem.* **1975**, *14*, 541–6. Haymore, B. L. *J. Organomet. Chem.* **1977**, *137*, C11–5.

(4) Bowden, W. L.; Little, W. F.; Meyer, T. J. *J. Am. Chem. Soc.* **1973**, *95*, 5084–5. Dart, J. W.; Lloyd, M. K.; Mason, R.; McCleverty, J. A. *J. Chem. Soc., Dalton Trans.* **1973**, 2039–45. Garner, A. W. B.; Mays, M. J. *J. Organomet. Chem.* **1974**, *67*, 153–60. N. G. Connelly, Demidowicz, Z. *Ibid.* **1974**, *73*, C31–2. Brownlee, G. S.; Carty, P.; Cash, D. N.; Walker, A. *Inorg. Chem.* **1975**, *14*, 323–7. Haymore, B. L.; Ibers, J. A. *Ibid.* **1975**, *14*, 2784–95.

(5) (a) Cowie, M.; Haymore, B. L.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 7608–17. (b) Carroll, J. A.; Cobbledick, R. E.; Einstein, F. W. B.; Farrell, N.; Sutton, D.; Vogel, P. L. *Inorg. Chem.* **1977**, *16*, 2462–9. Rattray, A. D.; Sutton, D. *Inorg. Chim. Acta* **1978**, *27*, L85–6.

(6) (a) Avitabile, G.; Ganis, P.; Nemiroff, M. *Acta Crystallogr., Sect. B* **1971**, *27*, 725–31. (b) Gaughan, A. P., Jr.; Haymore, B. L.; Ibers, J. A.; Meyers, W. H.; Nappier, T. E.; Meek, D. W. *J. Am. Chem. Soc.* **1973**, *95*, 6859–61.

(7) Laing, K. R.; Robinson, S. D.; Uttley, M. F. *J. Chem. Soc., Dalton Trans.* **1973**, 2713–22. Laing, K. R.; Robinson, S. D.; Uttley, M. F. *J. Chem. Soc., Chem. Commun.* **1973**, 176–7.

(8) Cowie, M.; Haymore, B. L.; Ibers, J. A. *Inorg. Chem.* **1975**, *14*, 2617–23. Haymore, B. L.; Ibers, J. A. *Ibid.* **1975**, *14*, 1369–76. Haymore, B. L.; Ibers, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 5369–79.

(9) Parshall, G. W. *J. Am. Chem. Soc.* **1965**, *87*, 2133–6; **1967**, *89*, 1822–6. Ittel, S. D.; Ibers, J. A. *Ibid.* **1974**, *96*, 4804–9. Ittel, S. D.; Ibers, J. A. *Inorg. Chem.* **1975**, *14*, 636–40.

0020-1669/80/1319-1231$01.00/0