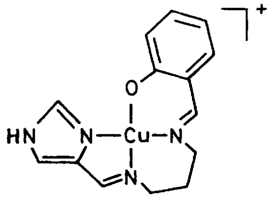
# Synthesis and *X*-Ray Crystal Structures† of an Imidazolate-bridged Polynuclear Copper(II) Complex exhibiting a Unique Helicoid Structure and its Precursor Mononuclear Complex

**Naohide Matsumoto,* Sadatoshi Yamashita, and Akira Ohyoshi**
*Department of Applied Chemistry, Faculty of Engineering, Kumamoto University, Kurokami 2-39-1, Kumamoto 860, Japan*
**Susumu Kohata**
*Yatsushiro National College of Technology, Yatsushiro 866, Japan*
**Hisashi Ōkawa**
*Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812, Japan*

The mononuclear copper(II) complex with the unsymmetrical quadridentate ligand [(4-imidazolyl)methyliminopropylsalicylideneiminato]copper(II) tetraphenylborate, $[Cu(HL)][BPh_4]$, has been prepared and characterized. The complex deprotonates the imidazole proton in the presence of triethylamine to produce the imidazolate-bridged polynuclear complex $[(CuL)_n]$. The structures of both complexes have been established by single-crystal *X*-ray diffraction analyses. The mononuclear complex crystallizes in the monoclinic space group $P2_1/n$ with $a$ = 20.822(4), $b$ = 14.132(3), $c$ = 10.698(2) Å, β = 98.63(2)°, and $Z$ = 4. The copper atom assumes a square-planar co-ordination environment with a slight distortion toward tetrahedral, where the dihedral angle between the $CuN_2$ and CuON planes representing the degree of tetrahedral distortion is 10.9°. The polynuclear complex crystallizes in the triclinic space group $P\bar{1}$ with $a$ = 15.421(5), $b$ = 16.594(4), $c$ = 10.537(1) Å, α = 115.08(1), β = 103.21(2), γ = 57.48(2)°, and $Z$ = 2. The complex has a unique helicoid linear-chain structure along the $c$ axis formed by the imidazolate bridges, where the copper atom assumes a square-based pyramidal co-ordination environment with the imidazolate nitrogen of the neighbouring copper complex occupying the axial position. The magnetic properties of the complex are well represented by the Ising model on the basis of a linear-chain structure.

Studies on polynuclear metal complexes including one-dimensional systems are very active fields of inorganic chemistry and solid-state physics. Previously, we have shown that the metal complexes of unsymmetrical quadridentate Schiff bases involving an imidazole ring function as ligands at the deprotonated imidazolate nitrogen toward a dissimilar second metal complex to form discrete homo- and hetero-metal binuclear complexes.[1] The principle of the synthetic method may be developed for constructing one-dimensional linear-chain assemblies, if the starting complex is designed so that it can expand its co-ordination number, under alkaline conditions, by bridging donation of an imidazolate group incorporated into the ligand.

In this study, we have adopted [(4-imidazolyl)methyliminopropylsalicylideneiminato]copper(II) tetraphenylborate, $[Cu(HL)][BPh_4]$, as such a complex and obtained a polymeric complex $[(CuL)_n]$ from $[Cu(HL)][BPh_4]$ in alkaline medium. We report here the crystal structure and magnetic properties of $[(CuL)_n]$, which has a unique helicoid linear-chain structure formed by imidazolate bridges, together with the crystal structure of the precursor complex $[Cu(HL)][BPh_4]$.



$[Cu(HL)]^+$

## Experimental

*Synthesis.*—$[Cu(HL)][ClO_4]$. The copper(II) complex with the 1 : 1 : 1 condensation product of salicylaldehyde, 1,3-propanediamine, and 4-formylimidazole was prepared as follows. The complex bis(3-aminopropylsalicylideneiminato)nickel(II) was prepared by the method of Elder.[2] A solution of the ligand was obtained by refluxing the nickel(II) complex with two equivalents of dimethylglyoxime in methanol for 2 h and filtering out precipitated bis(dimethylglyoximato)nickel(II), according to the procedure of Burke and McMillin.[3] To the ligand solution was added one equivalent of 4-formylimidazole[4] and the mixture was warmed at 50 °C for 1 h and cooled to ambient temperature. To the solution was added a solution of copper(II) perchlorate hexahydrate in methanol to precipitate immediately moss-green fine crystals. They were collected by suction filtration and washed with methanol. The complex was recrystallized from methanol-*N*,*N*-dimethylformamide (dmf) (*ca.* 10:1 v/v). Yield *ca.* 70%, m.p. 305 °C (decomp.) (Found: C, 40.35; H, 3.65; N, 13.5. Calc. for $C_{14}H_{15}ClCuN_4O_5$: C, 40.2; H, 3.60; N, 13.4%). I.r.(Nujol): ν(NH) 3 300; ν(Cl–O) 1 060, 1 100 $cm^{-1}$. U.v.-visible spectrum in dmf, $\lambda_{max.}$/nm ($\varepsilon$/$dm^3$ $mol^{-1}$ $cm^{-1}$): 375 (5 300) and 590 (100).

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

$[Cu(HL)][BPh_4]$. The tetraphenylborate salt was prepared by a similar method as for the perchlorate salt except that copper(II) acetate monohydrate and sodium tetraphenylborate were used. The complex was recrystallized from methanol–dmf (*ca.* 10:1 v/v) to give black rhombic crystals suitable for *X*-ray diffraction study. Yield *ca.* 60%, m.p. 248 °C (decomp.) (Found: C, 71.35; H, 5.45; N, 8.95. Calc. for $C_{38}H_{35}BCuN_4O$: C, 71.55; H, 5.55; N, 8.80%). I.r. (Nujol): $\nu$(NH) 3 290; $BPh_4^-$ 710 $cm^{-1}$. U.v.–visible in dmf, $\lambda_{max.}$/nm ($\varepsilon_{max.}$/dm$^3$ mol$^{-1}$ cm$^{-1}$): 380 (5 200) and 590 (95); solid state: 560 and 700.

*Imidazolate-bridged polynuclear complex* $[(CuL)_n]$. Addition of sodium methoxide or triethylamine to a methanol–dmf (*ca.* 5:1) solution of $[Cu(HL)][BPh_4]$ caused the precipitation of a light green microcrystalline material. Yield *ca.* 80%. Crystals suitable for *X*-ray diffraction analysis were obtained as green prisms by a diffusion method, where a dmf solution of the complex $[Cu(HL)][BPh_4]$ and the methanol solution of sodium methoxide were used, m.p. 290 °C (decomp.) (Found: C, 52.5; H, 4.45; N, 17.3. Calc. for $C_{14}H_{14}CuN_4O$: C, 52.9; H, 4.45; N, 17.65%). U.v.–visible (solid state): 650 nm.

*Physical Measurements.*—Elemental analyses were performed by Mr. Shinichi Miyazaki at the Technical Service Center of Kumamoto University. Melting points were measured on a Yanagimoto micromelting points apparatus and were uncorrected. Infrared spectra were recorded as Nujol mulls with a JASCO A-702 spectrophotometer. The electronic spectra in solution were measured on a Hitachi 340 spectrophotometer; reflectance spectra of ground solid samples were measured on a Shimadzu UV 260 spectrophotometer. The magnetic susceptibilities were obtained by the Faraday method at liquid nitrogen temperature to ambient temperature. Susceptibilities were corrected for the diamagnetism of the component atoms using Pascal's constants.

*X-Ray Diffraction Analyses.*—Diffraction data were obtained on a Rigaku Denki AFC-5R four-circle diffractometer at the Institute for Molecular Science, Okazaki National Institute, for the complex $[Cu(HL)][BPh_4]$ and on a Rigaku Denki AFC-5 four-circle diffractometer at the Faculty of Science, Kyushu University, for the complex $[(CuL)_n]$ using graphite-monochromatized Mo-$K_\alpha$ radiation at ambient temperature (20 ± 1 °C). Pertinent crystallographic parameters are summarized in Table 1. Three standard reflections were monitored every 100 measurements and their intensities showed no decay. Reflection data were corrected for Lorentz polarization effects but not for absorption.

The structures were solved by the standard heavy-atom method and refined by block-diagonal least-squares methods. Reliability factors are defined as $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, where the weights were taken as $w = 1$. In the deprotonated complex $[(CuL)_n]$, the central carbon atoms of the saturated six-membered chelate rings are subject to disorder. The occupancy factors for two possible positions 0.6 [C(91)] and 0.4 [C(92)] were evaluated on the basis of the peak heights of the difference-Fourier synthesis. In both complexes, non-hydrogen atoms were refined anisotropically. Hydrogen atoms at calculated positions were included in the structure factor calculations but not refined. Final difference Fourier syntheses for both complexes were featureless (no peaks > 0.6 e Å$^{-3}$). Positional parameters for non-hydrogen atoms for the complexes $[Cu(HL)][BPh_4]$ and $[(CuL)_n]$ are given in Tables 2 and 3, respectively.

Calculations were carried out on the HITAC M 200H computer at the Computer Center of the Institute for Molecular Science for the complex $[Cu(HL)][BPh_4]$ and on the FACOM M 386s computer at the Computer Center of Kyushu University for $[(CuL)_n]$ with the Universal Crystallographic Computation Program System UNICS III.[5] Atomic scattering factors for non-hydrogen atoms were taken from ref. 6, and those of hydrogen atoms from Stewart *et al.*[7] Corrections were made for the effects of anomalous dispersion for non-hydrogen atoms in the structure factor calculations.

**Table 1.** Crystallographic parameters of $[Cu(HL)][BPh_4]$ and $[(CuL)_n]$

| | $[Cu(HL)][BPh_4]$ | $[(CuL)_n]$ |
|---|---|---|
| Formula | $C_{38}H_{35}BCuN_4O$ | $C_{42}H_{42}Cu_3N_{12}O_3$ |
| $M$ | 638.08 | 953.49 |
| Crystal system | Monoclinic | Triclinic |
| Space group | $P2_1/n$ | $P\bar{1}$ |
| $a$/Å | 20.822(4) | 15.421(5) |
| $b$/Å | 14.132(3) | 16.594(4) |
| $c$/Å | 10.698(2) | 10.537(1) |
| $\alpha$/° | 90.00 | 115.08(1) |
| $\beta$/° | 98.63(2) | 103.21(2) |
| $\gamma$/° | 90.00 | 57.48(2) |
| $U$/Å$^3$ | 3 112.4(13) | 2 059.4(12) |
| $Z$ | 4 | 2 |
| $D_c$/g cm$^{-3}$ | 1.362 | 1.538 |
| $D_m$/g cm$^{-3}$ | 1.36 | 1.54 |
| Crystal size (mm) | 0.2 × 0.3 × 0.4 | 0.2 × 0.3 × 0.2 |
| $\mu$(Mo-$K_\alpha$)/cm$^{-1}$ | 7.6 | 15.9 |
| $F$(000) | 1 332 | 978 |
| Diffractometer | Rigaku AFC-5R | Rigaku AFC-5 |
| Scan type | $\theta$–2$\theta$ | $\theta$–2$\theta$ |
| Scan width (°) | 1.2 + 0.5 tan$\theta$ | 1.2 + 0.5 tan$\theta$ |
| Scan speed (° min$^{-1}$) | 8 | 8 |
| 2$\theta$ Range (°) | 2—50 | 2.5—46 |
| Octant collected | $+h, +k, \pm l$ | $+h, \pm k, \pm l$ |
| No. of unique data | 2 750 | 4 746 |
| $R$ | 0.045 | 0.055 |
| $R'$ | 0.073 | 0.059 |

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, remaining bond distances and angles.

## Results and Discussion

Previously, we have reported the synthesis, characterization, and *X*-ray crystal structures of the metal complexes with unsymmetrical quadridentate Schiff bases involving an imidazole moiety $[Cu(HL^1)]^+$, $[Ni(HL^1)]^+$, and $[Cu(HL^2)]^+$, where $H_2L^1$ and $H_2L^2$ denote the ligands composed of the condensation products of acetylacetone, ethylenediamine or 1,3-propanediamine, and 4-formylimidazole with the mole ratio of 1:1:1.[1] These complexes deprotonate the imidazole proton under alkaline conditions to give the electrically neutral species. The deprotonated species are stable and fairly soluble in common organic solvents such as chloroform, acetone, and methanol and can function as neutral ligands toward a second metal complex to produce discrete imidazole-bridged homo- and hetero-metal binuclear complexes.[1] On the contrary, the present mononuclear complex with an unsymmetrical quadridentate ligand composed of salicylaldehyde, 1,3-propanediamine, and 4-formylimidazole, $[Cu(HL)][BPh_4]$, deprotonates the imidazole proton to produce a compound insoluble in common solvents of formula [CuL], when the complex $[Cu(HL)][BPh_4]$ is treated in alkaline medium.

The molar electrical conductivity of the complex $[Cu(HL)][BPh_4]$ is 45.6 S cm$^2$ mol$^{-1}$ in dmf, indicating that the complex is a 1:1 electrolyte.[8] This implies that the unsymmetrical ligand co-ordinates to copper(II) ion as an uninegative ligand and the imidazole proton exists in the complex $[Cu(HL)][BPh_4]$. The i.r. spectrum of $[Cu(HL)][BPh_4]$ shows the characteristic bands at 3 290 cm$^{-1}$

**Table 2.** Fractional atomic co-ordinates ( × $10^4$) of $[Cu(HL)][BPh_4]$

| Atom | *X/a* | *Y/b* | *Z/c* |
|---|---|---|---|
| Cu | 767(1) | 417(1) | 586(1) |
| O | 26(2) | 286(3) | 1 411(4) |
| N(1) | 1 237(3) | −667(4) | 1 391(6) |
| N(2) | 1 478(3) | 789(4) | −459(6) |
| N(3) | 435(3) | 1 677(4) | −70(6) |
| N(4) | −38(3) | 2 980(4) | −797(6) |
| C(1) | −6(3) | −241(5) | 2 426(6) |
| C(2) | −543(4) | −137(6) | 3 057(7) |
| C(3) | −620(4) | −700(6) | 4 077(7) |
| C(4) | −153(4) | −1 372(6) | 4 519(8) |
| C(5) | 383(4) | −1 474(6) | 3 954(7) |
| C(6) | 474(3) | −913(5) | 2 901(7) |
| C(7) | 1 051(3) | −1 088(5) | 2 351(7) |
| C(8) | 1 842(4) | −1 027(6) | 979(8) |
| C(9) | 2 294(4) | −307(7) | 881(10) |
| C(10) | 2 064(4) | 220(6) | −554(9) |
| C(11) | 1 372(4) | 1 555(6) | −1 081(7) |
| C(12) | 797(4) | 2 079(5) | −918(7) |
| C(13) | 501(4) | 2 898(6) | −1 373(8) |
| C(14) | −60(4) | 2 240(5) | −30(7) |
| B | 1 979(4) | −4 441(6) | −169(8) |
| C(15) | 2 325(3) | −5 486(5) | −196(6) |
| C(16) | 2 756(4) | −5 649(5) | −1 080(7) |
| C(17) | 3 037(4) | −6 519(6) | −1 196(7) |
| C(18) | 2 921(4) | −7 279(5) | −449(7) |
| C(19) | 2 519(4) | −7 141(5) | 438(7) |
| C(20) | 2 228(3) | −6 259(5) | 567(7) |
| C(21) | 2 564(3) | −3 649(5) | 89(6) |
| C(22) | 3 007(4) | −3 673(6) | 1 217(7) |
| C(23) | 3 501(4) | −3 016(6) | 1 521(8) |
| C(24) | 3 594(4) | −2 315(6) | 687(9) |
| C(25) | 3 197(4) | 2 294(5) | −463(9) |
| C(26) | 2 687(4) | 2 945(5) | −753(7) |
| C(27) | 1 506(3) | 4 236(5) | −1 522(6) |
| C(28) | 1 165(3) | 3 382(5) | −1 699(6) |
| C(29) | 740(4) | −3 182(6) | −2 777(7) |
| C(30) | 635(4) | −3 825(6) | −3 759(7) |
| C(31) | 960(4) | −4 664(6) | −3 632(7) |
| C(32) | 1 387(4) | −4 868(5) | −2 530(7) |
| C(33) | 1 498(3) | −4 425(4) | 924(6) |
| C(34) | 1 579(3) | −3 882(5) | 2 021(7) |
| C(35) | 1 176(4) | −3 974(6) | 2 943(6) |
| C(36) | 669(3) | −4 602(6) | 2 796(7) |
| C(37) | 554(3) | −5 130(5) | 1 711(7) |
| C(38) | 956(3) | −5 033(5) | 789(7) |

**Table 3.** Fractional atomic co-ordinates ( × $10^4$) of $[(CuL)_n]$

| Atom | *X/a* | *Y/b* | *Z/c* |
|---|---|---|---|
| Cu(A) | 311(1) | 749(1) | 4 147(1) |
| O(A) | −338(4) | 1 827(4) | 5 901(5) |
| N(A1) | −965(5) | 706(5) | 3 378(7) |
| N(A2) | 1 232(4) | −642(4) | 2 664(5) |
| N(A3) | 1 669(4) | 453(4) | 5 063(6) |
| N(A4) | 3 105(4) | 151(4) | 6 361(6) |
| C(A1) | −1 314(6) | 2 412(6) | 6 164(8) |
| C(A2) | −1 636(7) | 3 244(7) | 7 481(10) |
| C(A3) | −2 646(8) | 3 893(8) | 7 830(13) |
| C(A4) | −3 393(8) | 3 759(8) | 6 866(16) |
| C(A5) | −3 126(7) | 2 956(7) | 5 603(13) |
| C(A6) | −2 074(6) | 2 258(6) | 5 221(9) |
| C(A7) | −1 857(6) | 1 398(6) | 3 924(8) |
| C(A8) | −936(8) | −146(9) | 2 060(11) |
| C(A91)[a] | −251(11) | −485(11) | 1 076(11) |
| C(A92)[b] | −125(18) | −1 055(16) | 1 513(22) |
| C(A10) | 912(6) | −1 184(6) | 1 305(7) |
| C(A11) | 2 177(6) | −1 052(6) | 3 000(7) |
| C(A12) | 2 457(5) | −489(5) | 4 336(6) |
| C(A13) | 3 340(6) | −679(6) | 5 138(7) |
| C(A14) | 2 083(5) | 821(5) | 6 280(7) |
| Cu(B) | 3 940(1) | 312(1) | 8 398(1) |
| O(B) | 3 513(4) | −339(4) | 9 078(5) |
| N(B1) | 5 256(4) | −962(5) | 7 669(6) |
| N(B2) | 4 411(4) | 1 227(4) | 8 306(5) |
| N(B3) | 2 880(4) | 1 669(4) | 9 616(5) |
| N(B4) | 1 749(4) | 3 100(4) | 11 205(6) |
| C(B1) | 3 905(6) | −1 317(5) | 8 743(8) |
| C(B2) | 3 393(7) | −1 631(7) | 9 244(10) |
| C(B3) | 3 748(8) | −2 641(8) | 8 939(14) |
| C(B4) | 4 638(9) | −3 398(8) | 8 124(16) |
| C(B5) | 5 170(8) | −3 124(7) | 7 650(12) |
| C(B6) | 4 808(6) | −2 066(5) | 7 971(8) |
| C(B7) | 5 457(6) | −1 855(6) | 7 524(8) |
| C(B8) | 6 081(7) | −930(8) | 7 218(13) |
| C(B91)[a] | 5 748(9) | −270(10) | 6 553(12) |
| C(B92)[b] | 6 187(15) | −123(17) | 7 559(21) |
| C(B10) | 5 272(6) | 913(6) | 7 478(8) |
| C(B11) | 3 878(5) | 2 178(6) | 9 054(7) |
| C(B12) | 3 032(5) | 2 462(5) | 9 826(7) |
| C(B13) | 2 340(5) | 3 339(5) | 10 821(7) |
| C(B14) | 2 094(5) | 2 089(5) | 10 458(7) |
| Cu(C) | 750(1) | 3 939(1) | 13 086(1) |
| O(C) | 1 826(4) | 3 515(4) | 14 416(5) |
| N(C1) | 698(5) | 5 262(4) | 13 631(6) |
| N(C2) | −644(4) | 4 411(4) | 12 073(6) |
| N(C3) | 453(4) | 2 873(4) | 12 935(6) |
| N(C4) | 152(4) | 1 746(4) | 13 106(6) |
| C(C1) | 2 418(6) | 3 899(6) | 15 069(8) |
| C(C2) | 3 235(6) | 3 397(7) | 15 871(9) |
| C(C3) | 3 903(8) | 3 753(8) | 16 572(13) |
| C(C4) | 3 769(9) | 4 642(9) | 16 518(15) |
| C(C5) | 2 961(8) | 5 166(8) | 15 768(12) |
| C(C6) | 2 256(6) | 4 813(6) | 15 035(8) |
| C(C7) | 1 402(6) | 5 459(6) | 14 384(8) |
| C(C8) | −144(9) | 6 086(7) | 13 162(12) |
| C(C91)[a] | −465(11) | 5 737(9) | 11 819(13) |
| C(C92)[b] | −1 059(15) | 6 184(13) | 12 669(22) |
| C(C10) | −1 189(7) | 5 273(6) | 11 570(8) |
| C(C11) | −1 059(6) | 3 877(5) | 11 879(7) |
| C(C12) | −498(5) | 3 038(5) | 12 371(6) |
| C(C13) | −685(6) | 2 343(5) | 12 480(7) |
| C(C14) | 816(5) | 2 098(5) | 13 372(7) |

[a] Occupancy factor 0.6. [b] Occupancy factor 0.4.

due to the imidazole-proton stretching vibration and at 710 cm$^{-1}$ due to the counter anion $BPh_4^-$, while these bands disappear in the spectrum of the complex treated with alkali. This gives evidence that the imidazole proton of the precursor complex $[Cu(HL)][BPh_4]$ is deprotonated to give the product [CuL]. Reflectance spectra suggest that the complexes $[Cu(HL)][BPh_4]$ and [CuL] have different co-ordination geometries. The spectrum of $[Cu(HL)][BPh_4]$ shows a broad

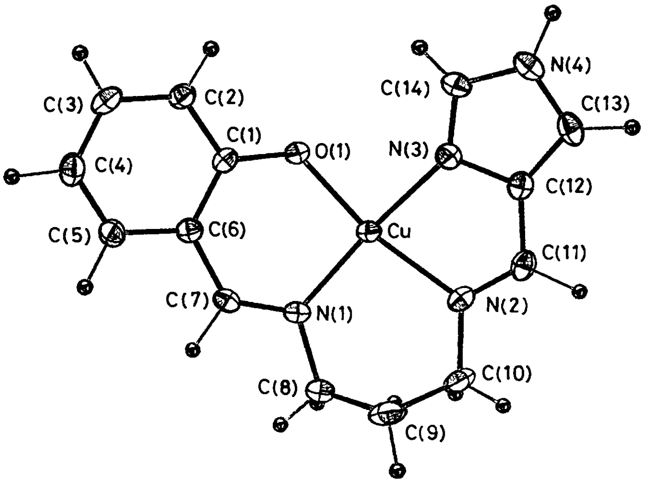


**Figure 1.** Molecular structure of [Cu(HL)]$^+$ with the atom numbering scheme

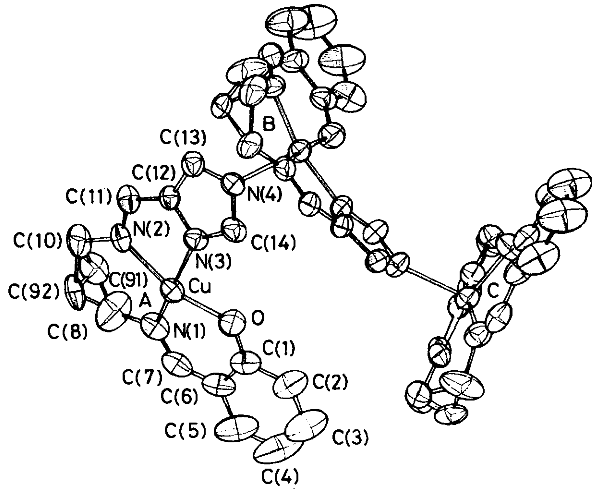


**Figure 2.** Molecular structure of [(CuL)$_n$] with the atom numbering scheme, where the asymmetric unit of the crystal structure is drawn and hydrogen atoms are omitted for clarity

band at 560 nm and a shoulder at 700 nm in the visible region assignable to *d–d* transitions, while that of [CuL] shows a broad band at 650 nm.

*Structural Description*.—Perspective views of the cation of the mononuclear complex [Cu(HL)]$^+$ and the polynuclear complex [(CuL)$_n$] are shown in Figures 1 and 2, which employ the same atom numbering system. Relevant bond distances and angles with their estimated standard deviations in parentheses are given in Tables 4 and 5.

[Cu(HL)][BPh$_4$]. The copper atom assumes a square-planar co-ordination geometry with a slight tetrahedral distortion, where the dihedral angle between the CuON(1) and CuN(2)N(3) planes, representing a degree of distortion from square planar to tetrahedral, is 10.9°. It should be noted that the co-ordination geometries of the complexes [Cu(HL$^1$)][ClO$_4$] and [Cu(HL$^2$)][ClO$_4$] are square planar and show no distortion toward tetrahedral.[1] It should be also noted that the Cu–donor atom bond distances of [Cu(HL)][BPh$_4$] are longer than those of [Cu(HL$^1$)][ClO$_4$] and [Cu(HL$^2$)][ClO$_4$].[1] The saturated six-membered chelate ring has a chair conformation, where the atoms Cu and C(9) deviate −0.18 and 0.71 Å from the mean plane defined by the atoms N(1), N(2), C(8), and C(10).

**Table 4.** Relevant bond distances (Å)[a] for [Cu(HL)][BPh$_4$] and [(CuL)$_n$]

| | | [(CuL)$_n$] | | |
|---|---|---|---|---|
| | [Cu(HL)]$^+$ | A | B | C |
| Cu–O(1) | 1.910(5) | 1.934(4) | 1.936(8) | 1.931(5) |
| Cu–N(1) | 1.951(5) | 1.978(7) | 1.977(5) | 1.979(8) |
| Cu–N(2) | 2.038(6) | 2.054(4) | 2.045(9) | 2.056(5) |
| Cu–N(3) | 1.993(5) | 1.984(5) | 1.986(4) | 1.990(8) |
| O(1)–C(1) | 1.327(8) | 1.296(8) | 1.295(10) | 1.295(11) |
| C(1)–C(2) | 1.397(10) | 1.426(10) | 1.429(19) | 1.407(11) |
| C(2)–C(3) | 1.384(11) | 1.359(13) | 1.358(16) | 1.376(17) |
| C(3)–C(4) | 1.381(11) | 1.399(17) | 1.404(16) | 1.399(23) |
| C(4)–C(5) | 1.362(11) | 1.369(15) | 1.382(25) | 1.378(17) |
| C(5)–C(6) | 1.417(10) | 1.421(11) | 1.426(14) | 1.427(16) |
| C(1)–C(6) | 1.420(9) | 1.415(12) | 1.395(9) | 1.414(15) |
| C(6)–C(7) | 1.432(10) | 1.434(10) | 1.443(16) | 1.431(10) |
| N(1)–C(7) | 1.279(9) | 1.283(9) | 1.285(12) | 1.298(12) |
| N(1)–C(8) | 1.487(10) | 1.492(12) | 1.490(17) | 1.473(12) |
| C(8)–C(9) | 1.458(12) | 1.370(21) | 1.354(22) | 1.370(16) |
| C(8)–C(9′) | | 1.318(19) | 1.322(33) | 1.332(25) |
| C(9)–C(10) | 1.524(13) | 1.558(14) | 1.580(14) | 1.588(23) |
| C(9′)–C(10) | | 1.552(32) | 1.553(22) | 1.549(22) |
| N(2)–C(10) | 1.475(10) | 1.472(9) | 1.484(12) | 1.476(11) |
| N(2)–C(11) | 1.271(10) | 1.271(9) | 1.278(7) | 1.278(14) |
| C(11)–C(12) | 1.438(11) | 1.444(9) | 1.444(12) | 1.438(11) |
| C(12)–C(13) | 1.368(10) | 1.380(9) | 1.381(7) | 1.381(15) |
| N(3)–C(12) | 1.385(10) | 1.369(6) | 1.376(12) | 1.375(9) |
| N(3)–C(14) | 1.307(9) | 1.343(8) | 1.343(10) | 1.337(11) |
| N(4)–C(13) | 1.365(11) | 1.365(7) | 1.360(14) | 1.369(9) |
| N(4)–C(14) | 1.332(10) | 1.365(8) | 1.352(8) | 1.356(13) |
| Cu–N(4) | | 2.230(8)[b] | 2.226(5) | 2.235(6) |

[a] Estimated standard deviations are given in parentheses. [b] Translation is operated to N(C4).

[(CuL)$_n$]. The *X*-ray analysis verified a unique helicoid linear-chain structure formed by imidazolate bridges. The crystal structure projected on the *bc* and *ab* planes is shown in Figure 3. The asymmetric unit of the crystal comprises three copper units A, B, and C. The imidazolate nitrogen atom N(A4) of unit A co-ordinates to the copper(II) ion Cu(B) of unit B, the imidazolate nitrogen atom N(B4) of unit B co-ordinates to the copper(II) ion Cu(C) of unit C, the imidazolate nitrogen atom N(C4) of unit C co-ordinates to the copper(II) ion Cu(A*) of unit A* [*c* translation is operated to Cu(A); *x*, *y*, *z* + 1], and such imidazolate bridges are repeated. As a result, a unique helicoid linear-chain structure is produced.

The copper(II) ions in all units assume the same geometries in bond distances and angles within experimental error. Each copper(II) ion assumes a square-based pyramidal co-ordination environment with the imidazolate nitrogen atom of the neighbouring copper unit occupying the axial position. In the square-based pyramidal geometry, the copper atom deviates by 0.18 Å toward the imidazolate nitrogen atom. The Cu–N(imidazolate) bond distances are 2.226(5) for Cu(B)–N(A4), 2.235(6) for Cu(C)–N(B4), and 2.230(8) Å for Cu(A*)–N(C4). These bond distances are longer than the corresponding values of imidazolate-bridged polynuclear complexes.[9–13] The central carbon atoms of saturated six-membered chelate rings in all copper units are subject to disorder. The occupancy factors for two possible positions C(91) and C(92) are estimated to be 0.6 and 0.4, respectively. The chelate ring involving the atom C(91) adopts a boat conformation, that involving C(92) a chair conformation.

**Table 5.** Relevant bond angles (°)* for $[Cu(HL)][BPh_4]$ and $[(CuL)_n]$

| | $[Cu(HL)]^+$ | $[(CuL)_n]$ | | |
|---|---|---|---|---|
| | | A | B | C |
| O(1)–Cu–N(1) | 95.5(2) | 92.8(2) | 92.9(2) | 93.1(2) |
| N(1)–Cu–N(2) | 95.2(2) | 93.6(2) | 93.4(2) | 93.1(2) |
| N(2)–Cu–N(3) | 80.2(2) | 80.3(2) | 80.5(2) | 80.3(2) |
| O(1)–Cu–N(3) | 89.1(2) | 88.8(2) | 88.7(2) | 89.0(2) |
| Cu–O(1)–C(1) | 125.7(4) | 127.2(4) | 126.7(5) | 127.6(6) |
| O(1)–C(1)–C(2) | 118.5(6) | 118.1(7) | 117.2(6) | 118.3(9) |
| O(1)–C(1)–C(6) | 123.3(6) | 123.3(6) | 123.8(10) | 122.5(6) |
| C(2)–C(1)–C(6) | 118.0(6) | 118.4(7) | 118.8(8) | 119.0(9) |
| C(1)–C(2)–C(3) | 121.0(6) | 121.6(9) | 121.2(9) | 121.4(11) |
| C(2)–C(3)–C(4) | 120.8(7) | 119.4(9) | 120.0(15) | 120.1(10) |
| C(3)–C(4)–C(5) | 119.7(7) | 121.3(9) | 120.5(12) | 119.9(13) |
| C(4)–C(5)–C(6) | 121.1(7) | 120.2(9) | 119.9(8) | 120.9(13) |
| C(1)–C(6)–C(5) | 119.0(6) | 118.8(7) | 119.4(11) | 118.4(8) |
| C(1)–C(6)–C(7) | 123.9(6) | 124.2(6) | 124.7(8) | 125.2(9) |
| C(5)–C(6)–C(7) | 116.9(6) | 116.8(8) | 115.7(7) | 116.1(9) |
| N(1)–C(7)–C(6) | 127.6(6) | 126.1(8) | 125.6(6) | 125.8(9) |
| Cu–N(1)–C(7) | 122.0(5) | 123.8(5) | 123.8(6) | 123.1(5) |
| Cu–N(1)–C(8) | 121.5(4) | 120.2(5) | 120.3(6) | 121.3(6) |
| C(7)–N(1)–C(8) | 116.3(6) | 115.8(7) | 115.8(6) | 115.4(8) |
| N(1)–C(8)–C(9) | 115.4(7) | 114.9(13) | 115.1(8) | 113.8(8) |
| N(2)–C(8)–C(9′) | | 126.6(13) | 127.6(11) | 127.1(15) |
| C(8)–C(9)–C(10) | 113.5(6) | 118.3(11) | 117.6(9) | 117.4(14) |
| C(8)–C(9′)–C(10) | | 122.2(23) | 121.7(17) | 122.6(11) |
| N(2)–C(10)–C(9) | 111.3(7) | 108.9(6) | 108.5(10) | 108.1(7) |
| N(2)–C(10)–C(9′) | | 108.1(9) | 108.4(13) | 108.7(10) |
| Cu–N(2)–C(10) | 124.7(5) | 127.3(4) | 127.6(4) | 127.4(6) |
| Cu–N(2)–C(11) | 114.6(5) | 114.0(4) | 114.2(6) | 113.9(5) |
| C(10)–N(2)–C(11) | 120.5(6) | 118.6(5) | 118.0(8) | 118.6(6) |
| N(2)–C(11)–C(12) | 117.0(7) | 116.8(5) | 116.7(9) | 116.8(7) |
| N(3)–C(12)–C(11) | 114.6(6) | 115.3(5) | 115.1(5) | 115.5(8) |
| N(3)–C(12)–C(13) | 108.4(6) | 108.8(5) | 108.4(8) | 108.4(6) |
| C(11)–C(12)–C(13) | 136.9(7) | 135.6(5) | 136.3(9) | 135.9(7) |
| Cu–N(3)–C(12) | 113.0(4) | 113.2(4) | 113.1(5) | 112.9(5) |
| Cu–N(3)–C(14) | 140.2(5) | 140.4(4) | 140.9(6) | 140.5(5) |
| C(12)–N(3)–C(14) | 106.5(6) | 105.6(5) | 105.3(5) | 105.6(8) |
| C(13)–N(4)–C(14) | 108.4(6) | 105.8(5) | 106.1(6) | 105.8(8) |
| N(4)–C(13)–C(12) | 105.6(7) | 107.8(5) | 107.9(7) | 107.8(7) |
| N(3)–C(14)–N(4) | 110.9(7) | 111.7(4) | 112.1(8) | 112.2(6) |
| N(4)–Cu–O(1) | | 97.6(2) | 97.6(2) | 97.6(2) |
| N(4)–Cu–N(1) | | 96.4(3) | 96.1(2) | 96.4(3) |
| N(4)–Cu–N(2) | | 97.4(2) | 97.4(2) | 97.5(2) |
| N(4)–Cu–N(3) | | 100.2(2) | 100.4(2) | 100.1(2) |
| C(13)–N(4)–Cu | | 130.3(4) | 129.9(4) | 129.9(4) |
| C(14)–N(4)–Cu | | 121.2(3) | 121.4(6) | 121.6(3) |

* Estimated standard deviations are given in parentheses.

It is noteworthy to compare the structural parameters of the complexes $[Cu(HL)][BPh_4]$ and $[(CuL)_n]$. With respect to co-ordination geometry, the complex $[Cu(HL)][BPh_4]$ is square planar with a tetrahedral distortion, while $[(CuL)_n]$ assumes a square-based pyramidal geometry. Some bond distances and angles are obviously reflected by the differences in co-ordination geometry. The Cu–O bond distance of $[Cu(HL)][BPh_4]$ is shorter than that of $[(CuL)_n]$, and on the contrary, the C(1)–O bond distance is longer.

*Magnetic Properties.*—Plots of the temperature dependence of the magnetic susceptibility and the reciprocal magnetic susceptibility are shown in Figure 4. The plot of $1/\chi_A$ *vs.* $T$ is linear and obeys the Curie–Weiss law $[1/\chi_A = C(T + \theta)]$ with a Weiss constant of $\theta = 25$ K, which was obtained by a least-squares method; the maximum deviation of the observed $1/\chi_A$ from the calculated value is 3%. This suggests that intra- or/and inter-polymer antiferromagnetic interaction is operating. Since the inter-polymer magnetic interaction is negligible on the basis of the crystal structure, the intra-polymer interaction is operating. The magnetic susceptibility data were analysed on the basis of the Ising model for a one-dimensional infinite chain structure. The magnetic susceptibility expression is given in equation (1)

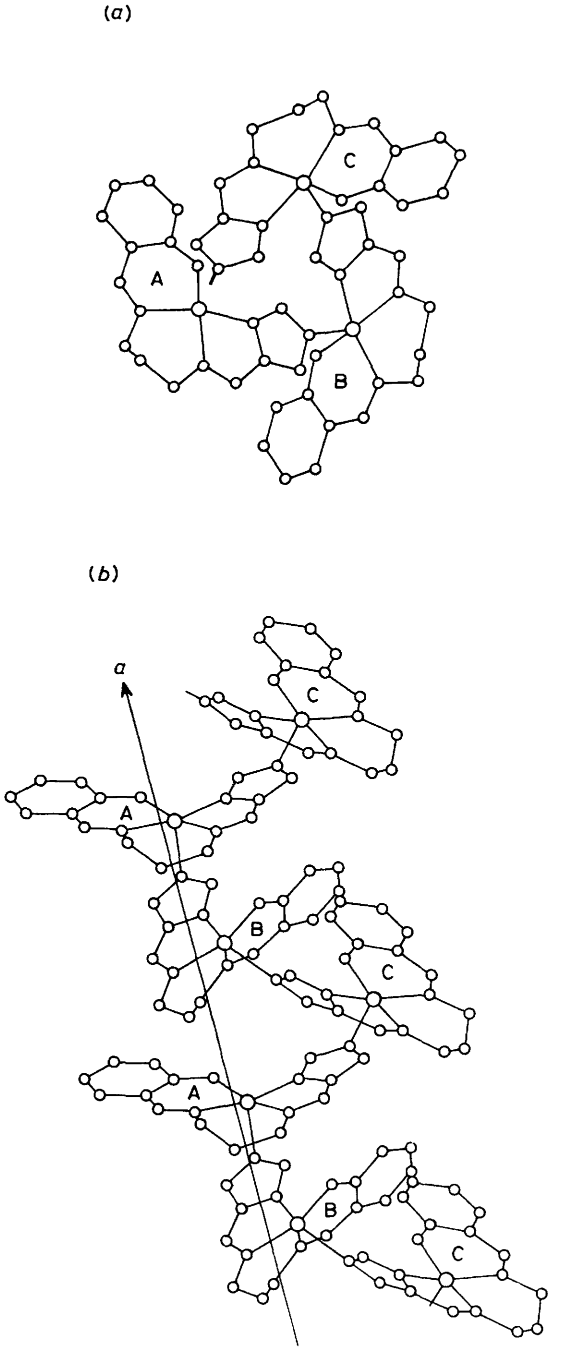


**Figure 3.** Crystal structure of $[(CuL)_n]$ projected on (*a*) the *bc* and (*b*) the *ab* planes

$$\chi_{av} = \frac{Ng^2\beta^2}{12kT}\,\frac{e^{4K} + (2 + K^{-1})e^{2K} - K^{-1}e^{-2K} + 5}{e^{2K} + e^{-2K} + 2} + N\alpha \qquad (1)$$

($K = J/kT$), where the spin-Hamiltonian in the form $\mathcal{H} = -2\Sigma J_{ij}\hat{S}_i\cdot\hat{S}_j$ is used.[14]

The temperature-independent paramagnetism ($N\alpha$) was

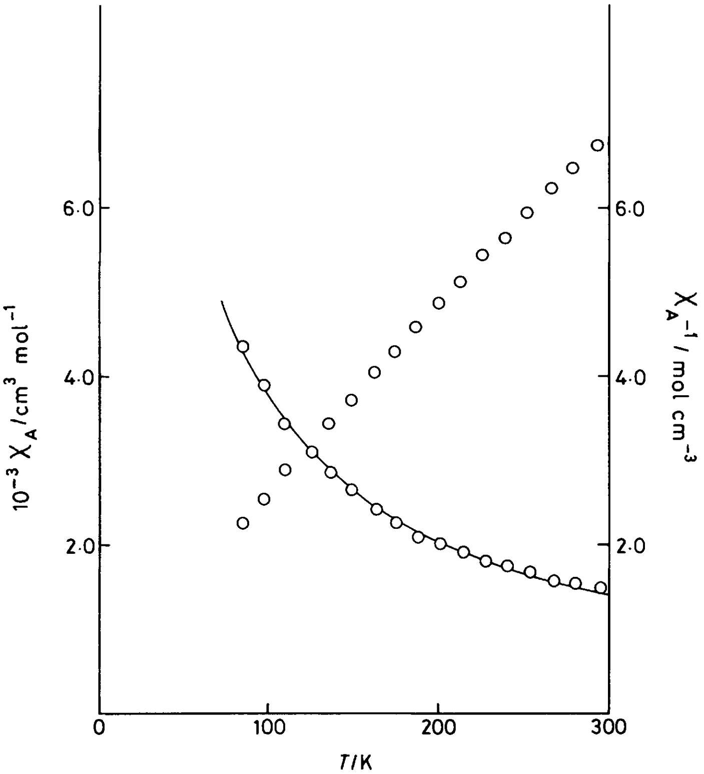


**Figure 4.** Plots of $\chi_A$ *vs.* $T$ and $1/\chi_A$ *vs.* $T$ for $[(CuL)_n]$

taken to be $60 \times 10^{-6}$ cm$^3$ mol$^{-1}$, while the other other symbols have their usual meanings. The observed susceptibility data were well reproduced by equation (1) with the parameters $g = 2.18$ and $2J = -30$ cm$^{-1}$, where the generalized $R$ factor, $R = \{\Sigma[\chi_A(\text{obs.}) - \chi_A(\text{calc.})]^2/\Sigma\chi_A(\text{obs.})^2\}^{\frac{1}{2}}$, used as a convenient statistical indicator of the quality of the fit, was $1.1 \times 10^{-4}$.

The coupling constant is relatively small compared to those of the imidazolate-bridged binuclear complexes.[1,9–13] The small coupling constant is presumably due to the long Cu–N(imidazolate) bond distance and almost perpendicular orientation between the basal co-ordination plane and the imidazolate ring plane. The other structural parameters $\alpha_1$ and $\alpha_2$ (the angles between the Cu–N and N–N vectors in the bridging imidazolate moiety)[15] are 172.0 and 152.7°, respectively. These values are smaller than those of the complexes $[CuL^1Cu\{O_2CCH_2C(O)CF_3\}_2]$ ($\alpha_1 = 176.4$, $\alpha_2 = 156.6°$) and $[CuL^1CuL']^{2+}$ [L′ = tris(2-*N*-ethylbenzimidazolylmethyl)amine] ($\alpha_1 = 176.9$, $\alpha_2 = 154.6°$).[1]

## Acknowledgements

We thank the Institute for Molecular Science (Instrument Center) and Professor Sigeo Kida for use of the *X*-ray diffractometer. We also thank the Computer Center of the Institute for Molecular Science for facilities. This work was supported in part by a grant-in-aid (to N. M.) for scientific research from the Ministry of Education, Science and Culture, Japan.

## References

1 N. Matsumoto, T. Akui, H. Murakami, J. Kanesaka, A. Ohyoshi, and H. Ōkawa, *J. Chem. Soc., Dalton Trans.*, 1988, 1021; N. Matsumoto, H. Murakami, T. Akui, J. Honbo, H. Ōkawa, and A. Ohyoshi, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 1609; N. Matsumoto, J. Kanesaka, M. Nakamura, S. Kohata, A. Ohyoshi, and H. Ōkawa, *ibid.*, 1987, **60**, 3056.
2 R. C. Elder, *Aust. J. Chem.*, 1978, **31**, 35.
3 P. J. Burke and D. R. McMillin, *J. Chem. Soc., Dalton Trans.*, 1980, 1794.
4 'Organic Syntheses,' Wiley, New York, 1955, col. vol. 3, p. 460; R. A. Turner, C. F. Heubner, and C. R. Scholz, *J. Am. Chem. Soc.*, 1949, **71**, 2802; E. Papadopoluos, A. Jarrar, and C. H. Issidarides, *J. Org. Chem.*, 1966, **31**, 615.
5 T. Sakurai and K. Kobayashi, *Rikagaku Kenkyusho Houkoku*, 1979, **55**, 69; S. Kawano, *Rep. Comput. Cent. Kyushu Univ.*, 1980, **13**, 39.
6 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
7 R. F. Stewart, E. R. Davison, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.
8 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.
9 J. P. Costes, J. F. Serra, F. Dahan, and J. P. Laurent, *Inorg. Chem.*, 1986, **25**, 2790.
10 C. L. O'Young, J. C. Dewan, H. R. Lilienthal, and S. J. Lippard, *J. Am. Chem. Soc.*, 1978, **100**, 7291.
11 M. G. B. Drew, M. McCann, and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1981, 1868.
12 J. C. Dewan and S. J. Lippard, *Inorg. Chem.*, 1980, **19**, 2079.
13 K. Matsumoto, S. Ooi, Y. Nakao, W. Mori, and A. Nakahara, *J. Chem. Soc., Dalton Trans.*, 1981, 2045.
14 E. Sinn, *Coord. Chem. Rev.*, 1970, **5**, 313.
15 A. Bencini, C. Benelli, D. Gatteschi, and C. Zanchini, *Inorg. Chem.*, 1986, **25**, 398.

*Received* 21*st July* 1987; *Paper* 7/1324