

# Anionic Amidinourea–Metal(II) Tautomers: MN<sub>2</sub>O<sub>2</sub> or MN<sub>4</sub>?

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Structures of amidinourea–metal complexes have been obscured by subtle tautomerism and crystal waters. To clarify the most stable form of the tautomers, bis(amidinourea)copper(II) anhydride and the alkyl derivatives were synthesized under basic conditions, and the stability of the  $CuN_2O_2$  chromophore was suggested. From substituent effects of chelations, UV–vis spectra, IR/Raman spectra, and DFT calculations, it was suggested that the bis(amidinourea)copper-(II) has a  $CuN_2O_2$  chromophore, not  $CuN_4$  chromophore. The mutual exclusion rule of IR/Raman spectra supported the *trans*- $CuN_2O_2$  chromophore. Systematic calculations on bis(amidinourea)–Cu(II), -Ni(II), -Pd(II), -Zn(II), and -Cd(II)chelates revealed that the robust stability of  $CuN_2O_2$  chromophores originates from quasi aromaticity in the six-membered chelate rings. *cis-* or *trans*- $CuN_4$  stability reported in the early references is suspicious.

Amidinourea (AU (1); the left-hand side of the top of Figure 1, often called guanylurea or 1-carbamoylguanidine) reacts with various metal ions to form stable complexes.<sup>1–8</sup> In early references, a tautomer shown in the right-hand side has been widely accepted as the most stable form. Nowadays, however, the correct form is found by X-ray analyses to be the Schiff-base type in the left-hand side.<sup>9</sup> Amidinourea derivatives (AUs) with alkyl substituents also react with various metal ions, especially in Cu<sup>2+</sup>. Recently, amidinothioureas have also been studied as related ligands.<sup>10</sup> AUs have been applied to designing metal-complexing agents.<sup>11,12</sup> Under weakly basic or weakly acidic conditions, AU is usually neutral, and all the hydrogen atoms combine with the branched nitrogens. In dilute



Figure 1. Molecular structures of amidinourea (AU; 1), *N*-methylamidinourea (2), *N*,*N*-dimethylamidinourea (3), *N*,*N'*-dimethylamidinourea (4), and *N*,*N*,*N'*-trimethyl-*N'*-benzylamidinourea (5).

aqueous solutions or polymer matrixes, AUs react with excess  $CuCl_2$  in a ratio 2:1 to form light-green complexes, in which  $Cu^{2+}$  is combined between two central nitrogen atoms of planar AU moieties, and two chloride ions coordinate to  $Cu^{2+}$  in the perpendicular direction.<sup>11</sup> In general, however, the coordination structures of AU-metal complexes have wide diversity. For example, as well as a special form above, Hubberstey et al. studied a coordinate structure of (neutral-AU)<sub>2</sub>-copper(II) dinitrate by X-ray analysis, and determined the chelate structures with a  $CuN_2O_2$  chromophore (Figure 2a).<sup>6</sup> In strongly



**Figure 2.** Possible molecular structures of bis-(amidinourea)copper(II) chelates. (a) is based on neutral AU. (b), (c), and (d) are based on anionic (deprotonated) AU.

acidic conditions, AU is also coordinated by a proton.<sup>7,9,11</sup> We denote it  $[AU + H]^+$ . This cationic moiety forms stable complexes with metal-containing counter anions, for example,  $[CuCl_4(H_2O)_2]^{2-.7}$  Given that there are many possible tautomers of AUs, determination of the coordination structures has been a subtle problem. The most stable isomer of each complex has been determined on a case-by-case basis.

Under basic conditions, on the other hand, AUs are subject to deprotonation by strong bases such as NaOH, and the resultant anionic moiety serves as a robust ligand for various metals. In this article, hereafter, the anionic ligand is denoted as  $[AU - H]^{-}$  (the minus symbol in the parenthesis means deprotonation). We must clearly distinguish neutral AU (simply denoted as AU), the cationic form  $[AU + H]^+$ , and the anionic form  $[AU - H]^{-}$ .  $[AU - H]^{-}$  forms a layender complex with Cu(II) in a ratio 2:1,<sup>2</sup> and the complexes often contain apparent crystal waters.<sup>7,8</sup> We note that in these cases there are no counter anions any more. For simplicity, we hereafter focus only on the anhydride form  $[AU - H]_2Cu$ . The standard synthetic method was established by Trimble.<sup>2</sup> As well as the  $[AU - H]_2Cu$  complex, he synthesized various amidinourea-metal and amidinothiourea-metal complexes under basic conditions.<sup>2</sup> However, the coordination structure of the complex [AU - H]<sub>2</sub>Cu has long been an open question due to insolubility to usual solvents (slightly soluble in aprotic solvent such as DMSO or DMF). A single crystal has not been obtained yet, and early workers speculated the coordination structure by mean of IR, vis (visible), and ESR spectra. An early IR study reported a CuN<sub>2</sub>O<sub>2</sub> chromophore with >C=O and  $>C=N^{-}$  groups,<sup>4</sup> but the rare valence of the nitrogen atoms was suspicious. Electrophilic substitution of the complex suggests the existence of imino groups -C=NH with quasi aromaticity,<sup>3</sup> and some vis-spectral studies concluded the presence of CuN<sub>4</sub> chromophore.<sup>7,8</sup> However, many early works including the references above were not sensitive to elimination of apparent crystal waters. This ambiguity has caused serious confusions for a long time. In particular, despite the fact that we cannot distinguish  $[AU - H]_2$ -Cu·2H<sub>2</sub>O and AU<sub>2</sub>Cu·(OH)<sub>2</sub> from the composition, the ESR hyperfine structures was formally attributed to the same CuN<sub>4</sub> chromophore.<sup>5,8</sup> In early references, charges of the ligands and the resultant change of the electronic states are often disregarded. Anyway, there has been no robust confirmation for the most stable coordination structure of the anionic AU complexes. As chemically reasonable structures, there are three coordination types, as shown in Figures 2b, 2c, and 2d. Figure 2b has a CuN<sub>2</sub>O<sub>2</sub> chromophore, and Figure 2c and Figure 2d have CuN<sub>4</sub> chromophores. Figure 2d is the proton-transferred tautomer of Figure 2c. Though Figure 2 shows only trans-isomers, there exists the corresponding *cis*-isomers for each coordination type. The detailed analysis of the coordination structure is important in that AU is a hybrid analogue of biuret and biguanide, of which Cu(II) complexes are well known in the field of biochemistry. Moreover, in view of application to metal-complexing agents,  $[AU - H]^-$  is a promising Lewis base as well as the neutral AUs. Indeed, we obtained anionic imino resins based on methacryloyl AU, and it has been found that the anionic AUs have highly selective adsorption efficiency for  $Cu^{2+}$ .<sup>12</sup>

In this paper, coordination structure of the 2:1 anhydride complex bis(amidinourea)copper(II) ( $[AU - H]_2Cu$ ) with lav-

ender color is investigated. The classical observation of this complex was reported by Trimble;<sup>2</sup> AU reacts with CuCl<sub>2</sub> in water in the presence of sodium potassium tartrate and NaOH to form a lavender complex. The Cu content has been reported to be 22.8%.<sup>2</sup> This value suggests that AU reacts with CuCl<sub>2</sub> in a ratio 2:1 and the complex does not contain chlorine atoms and/or crystal waters. Therefore, we should regard the AU moieties in this lavender complex as deprotonated anions. Although the complexation ratio is nearly evident from the Cu content, the coordination structure is not clear yet. Thus, the plausible coordination structures were investigated by means of UV-vis, IR spectra, Raman spectra, and DFT (density functional theory) calculations. The complexation ratio was reconfirmed by ICP analysis. The complex contains six-membered chelate rings, in which oxygen atoms of carbonyl groups and nitrogen atoms of imino groups plausibly participate in the coordination as depicted in Figure 2b. In addition, the IR/ Raman exclusion rule reveals the trans-type CuN<sub>2</sub>O<sub>2</sub> chromophore. Possible isomers with the carbamoyl-coordinated CuN<sub>4</sub> chromophore (Figure 2c) or tautomers with the proton transfered CuN<sub>4</sub> chromophore (Figure 2d) are plausibly eliminated from both experimental and theoretical points of views. The coordination structure is also confirmed by substituent effect on the complexation using substituted AUs; N-methylamidinourea (2), N.N-dimethylamidinourea (3), N.N'-dimethylamidinourea (4), and N,N,N'-trimethyl-N'-benzylamidinourea (5) shown in Figure 1. From the second-order perturbation theory and systematic calculations on bis(amidinourea)-Cu(II), -Ni(II), -Pd(II), -Zn(II), and -Cd(II) chelates, it is shown that the robust stability of the metal-N2O2 chromophore is attributed to quasi aromaticity of the  $6\pi$  chelate rings, in which the branched amino groups lower the energy of the systems through an extended topological charge stabilization rule.

## Experimental

AU was prepared by hydrolysis of cyanoguanidine as usual.<sup>11a</sup> The substituted AUs were kindly supplied by Shiba.<sup>11a</sup> They were identified by NMR spectrometer (Bruker DPX 300).

1: <sup>1</sup>HNMR (DMSO- $d_6$ ):  $\delta$  7.11 (s, 2H), 8.66 (s, 4H); <sup>13</sup>CNMR (DMSO- $d_6$ ):  $\delta$  161.29, 166.68.

**2**: <sup>1</sup>H NMR (DMSO- $d_6$ ):  $\delta$  2.84 (s, 3H), 7.19 (s, 2H), 8.61 (s, 3H); <sup>13</sup>C NMR (DMSO- $d_6$ ):  $\delta$  27.94, 154.63, 154.92.

**3**: <sup>1</sup>H NMR (DMSO- $d_6$ ):  $\delta$  2.87 (s, 6H), 5.51 (s, 2H), 7.81 (s, 2H); <sup>13</sup>C NMR (DMSO- $d_6$ ):  $\delta$  35.98, 160.28, 166.47.

**4**: <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ 2.78 (s, 6H), 6.51 (s, 2H), 7.65 (s, 2H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>): δ 27.43, 159.73, 165.85.

**5**: <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  2.64, (s, 3H), 2.77 (s, 6H), 4.31 (s, 2H), 5.55 (s, 2H), 7.31 (s, 5H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>):  $\delta$  39.04, 39.40, 54.70, 127.68, 128.27, 128.57, 135.78, 161.34, 163.25.

Bis(amidinoureas)copper(II) chelates ( $[AUs - H]_2Cu$ ) were prepared referring to the literature.<sup>2</sup> 1% (7.4 × 10<sup>-2</sup> mol L<sup>-1</sup>) CuCl<sub>2</sub> aqueous solution, 5% (0.24 mol L<sup>-1</sup>) sodium potassium tartrate (Rochelle salt) aqueous solution, 0.1 mol L<sup>-1</sup> aqueous AUs solution (in **5**, water/ethanol = 1:1 mixture was used as solvent because of the low solubility), and 5% (1.25 mol L<sup>-1</sup>) aqueous NaOH solutions were prepared using deionized and distilled water. 2 mL of each reagent was poured into a test tube in the named order. We note that Cu(OH)<sub>2</sub> is precipitated if sodium potassium tartrate is not added. Although the mixtures of CuCl<sub>2</sub>, sodium potassium tartrate, and aqueous AUs solutions were blue, addition of aqueous NaOH solution changed the color of the solutions into lavender. This lavender color is due to the imino-type  $[AUs - H]_2Cu$  complexes. It is known that  $[AU - H]_2Cu$  is insoluble in water or usual protic solvents. However, the UV-vis spectra of these supersaturated solutions could be recorded in a 10 mm cell by HITACHI U-4000 spectrophotometer.

After 3 days, lavender powder was precipitated from the solution of AU (1). This precipitate was washed with water and ethanol. The precipitate was filtered and dried under vacuum. The Cu content was confirmed by ICP analysis to be 23.75% (Calcd. 23.91%), which is consistent with that in the literature,<sup>2</sup> and the complexation ratio was confirmed to be 2:1. The IR spectrum was obtained by KBr-pellet using a JEOL JIR-RFX 3001 spectrometer. The Raman spectrum was recorded with a HORIBA/Jobin Yvon LabRAM HR-800 laser-Raman spectrometer. No precipitate formed from the solutions of substituted-AUs 2-5 even after 6 months.

#### **Results and Discussion**

Figure 3a shows UV spectrum of the  $[AU - H]_2Cu$  (solid line), together with that of neutral AU (dashed line). For  $[AU - H]_2Cu$ , the weak background of sodium potassium tartrate was calibrated. Figure 3b shows vis spectra of the reaction mixtures of 1-5 and CuCl<sub>2</sub> in the presence of sodium potassium tartrate and NaOH. While AU 1 has  $\pi - \pi^*$  absorption at 219 nm ( $\varepsilon = 12600 \,\text{M}^{-1} \,\text{cm}^{-1}$  in the presence of 0.01% NaOH), complexation with Cu<sup>2+</sup> results in blue shift of the  $\pi - \pi^*$  absorption at 205 nm ( $\varepsilon = 20700$ ) with a broad shoulder at 216 nm. The peak at 205 nm is consistent with that of Npropionylamidinourea anion (203 nm,  $\varepsilon = 20900$  at pH 10.9).<sup>12</sup> If the central nitrogen coordinates with metals or proton, the major peak for the  $\pi - \pi^*$  absorption should shift to the vacuum UV region.<sup>11,13</sup> Therefore, the  $\pi$ - $\pi$ \* absorption observed suggests that the Schiff-base moiety is conserved through the complexation. 1, 2, and 3 in which the N' positions of AU are not substituted by any group formed lavender complex solutions



Figure 3. (a) UV spectra of AU (dashed line) and bis-(amidinourea)copper(II) ( $[AU - H]_2Cu$ , solid line). (b) vis spectra of the reaction mixtures of 1-5 and CuCl<sub>2</sub> in the presence of sodium potassium tartrate and NaOH. 1, 2, and 3 form the lavender complexes. 4 and 5 do not form the complexes.

with  $\lambda_{\text{max}} = 582$ , 586, and 582 nm, respectively ( $\varepsilon = 40$ , Figure 3b). The role of Rochelle salt is not clear at present, but this probably serves as a catalyst and buffer for the complexation. Strictly speaking, we must discount the red-shift effects by residual Rochelle salt and Cu(II) ion. Indeed, in DMSO, the peak of pure  $[AU - H]_2Cu$  appeared with  $\lambda_{max} =$ 516 nm,  $\varepsilon = 40$ . The absorbance was essentially independent of temperature within 20-80 °C, which indicates robust stability of the complex. On the other hand, reaction mixtures of 4 and 5 in which the N' positions are substituted by methyl and/or benzyl groups did not form lavender complex solutions. The color of these solutions were blue with  $\lambda_{\text{max}} = 673$  and 672 nm, respectively. 4 and 5 should be neutral under the present conditions, and subject to complexation with CuCl<sub>2</sub><sup>11</sup> or Rochelle salt, if any. However, they are not important for our purpose. Thus, we can conclude from such substituent effects that N'-nitrogen atoms of AUs participate in the coordination. That is,  $OH^-$  deprotonates the N'-amino hydrogen atoms of AUs, and the resultant imino-type anions react with Cu<sup>2+</sup> in a ratio 2:1 to form lavender complexes.

Figure 4 shows IR and Raman spectra of  $[AU - H]_2Cu$ . Taking a closer look, IR peaks do not always correspond to the Raman peaks, particularly in the fingerprint region. Difference in IR/Raman spectra appears more clearly in metalligand vibrations than in ligand vibrations, because interactions between the vibrations are large in the fingerprint region. Indeed, as shown later, the mutual exclusion rule for the IR/ Raman spectra is clearly shown in the fingerprint region. Before the detailed assignment of the metal-ligand vibrations, we focus on the change of IR vibrations in the ligand moieties.





Figure 4. IR and Raman spectra of bis(amidinourea)copper(II) ( $[AU - H]_2Cu$ ).



Figure 5. IR spectra in the 4000–2500 and 2000–1200  $\text{cm}^{-1}$  regions. (a) AU (1) and (b) bis(amidinourea)copper-(II) ([AU - H]<sub>2</sub>Cu).

Figure 5 shows comparison of the zoomed IR spectra of AU (Figure 5a) and the  $[AU - H]_2Cu$  complex (Figure 5b). The peaks corresponding to N-H stretching of AU were observed at 3361 and 3222 cm<sup>-1</sup>. They are two broad bands. They are broadened by intermolecular association through the carbamoyl groups. We note that the intermolecular association through the carbamoyl groups lowers the wavenumbers of N-H stretching. Therefore, we should consider that the wavenumbers of N-H stretching of nonassociated AU are higher than those of the observed data. On the other hand, the peaks corresponding to N-H stretching of the [AU - H]<sub>2</sub>Cu complex were observed at 3403, 3363, 3352, and  $3197 \text{ cm}^{-1}$ . The peaks at 3403, 3363, and  $3352 \text{ cm}^{-1}$  are attributed to carbamovl-side-NH<sub>2</sub> groups. because they are more narrowed than those of AU by lifting the intermolecular association and the complexation. Indeed, some of these wavenumbers are higher than those of AU. The peak at 3197 cm<sup>-1</sup> is attributed to the imino groups formed by the deprotonation.

The peaks corresponding to C=O stretching were observed at 1635 cm<sup>-1</sup> in AU and 1622 cm<sup>-1</sup> in the  $[AU - H]_2Cu$  complex, respectively. The wavenumber of the complex was lower than that of AU. Given that the intermolecular association of AU lowers the wavenumber of C=O stretching and elongates the C=O bond length, we should consider that the wavenumber of C=O stretching of nonassociated AU is much higher than that of the observed data. Indeed, in a polymer matrix, the peak of C=O stretching in the nonassociated AU moiety is observed at 1734 cm<sup>-1.11</sup> Therefore, we can conclude that the C=O bond length of the  $[AU - H]_2Cu$  is longer than that of AU. In short, the oxygen atoms in carbonyl groups plausibly participate in the coordination, and the C=O bond length is elongated by the complexation.

In order to confirm the coordination structure described above, we performed DFT calculations on optimized structures of the complex. The calculations were done under unrestricted B3LYP/6-31G(d) and B3LYP/6-31G(d,p) level of theory<sup>14–16</sup> by using the Gaussian program.<sup>17</sup> Though the basis set impact on the optimized geometries and energetics was trivial, vibration analyses, and thermal corrections succeeded only at B3LYP/6-31G(d). Figure 6 shows optimized structures of the possible isomers of the 2:1 complex at B3LYP/6-31G(d) level of theory. The relative energies of each structure were also noted. Change of the zero-point energy and thermal corrections are sufficiently small to be neglected (details are attached in the Supporting Information.). We denote each structure as: trans- $CuN_2O_2$  (6), *cis*-CuN\_2O\_2 (7), *trans*-CuN<sub>4</sub> (8), *cis*-CuN<sub>4</sub> (9), proton-transferred trans-CuN<sub>4</sub> (10), and proton-transferred cis- $CuN_4$  (11). We can see that the *trans*-form chelate structure 6 with the  $CuN_2O_2$  chromophore is most stable. This is a nearly planar molecule with a  $C_2$  geometry. The calculated Cu–O and Cu-N bond lengths were 1.930 and 1.905 Å, respectively. The Cu-O bond length is comparable to that of typical ureascopper(II) complexes, for example, an X-ray analyzed complex between 5,5'-carbonylbis[1,3-dimethyl-3,4,5,6-tetrahydro-1,3,5-triazin-2(1H)-one] and CuCl<sub>2</sub> with 1.948 Å Cu-O distance.<sup>18</sup> The C=O bond length of the complex 6 was calculated to be 1.280 Å, which was longer than that of neutral AU (1.243 Å). This is consistent with the IR-spectra data. The N-Cu-O bond angles inside and outside the chelate ring were calculated to be 91.0 and 92.5°, respectively. Strictly speaking, the trans-isomer is not completely planar, as shown in the side views in Figure 6. However, for analyzing the IR/Raman spectra, it is convenient to regard the symmetry classification as  $C_{2h}$  approximately with an inversion center, as shown later. The cis-form chelate structure with CuN2O2 chromophore was slightly unstable  $(+4.1 \text{ kcal mol}^{-1})$  due to the steric hindrance between two hydrogens of the imino groups. The cis-CuN<sub>2</sub>O<sub>2</sub> form also has nearly a planar geometry, of which the point group is  $C_2 (= C_{2\nu})$ . On the other hand, there are two possible types of chelate structures with CuN4 chromophores, as shown in the bottom of Figure 6. One is the complex of which imino -NH and carbamoyl -NH<sub>2</sub> groups participate in the coordination, and another is the proton-transferred tautomer of which central nitrogens are saturated. However, these were unstable both in trans- and cis-forms. In particular, the amino coordination is very unstable. This is reminiscent of large proton affinity of imino sites in biguanide and polyguanide. 19,20

Imino-coordination preference is essentially attributed to large delocalization energy of the  $\pi$  electrons, as suggested from classical resonance structures. In the proton transferred form, however, the saturated central nitrogen atom causes less delocalization of the itinerant electrons in the AU moieties, similar to  $[AU + H]^+$  or diprotonated biguanide.<sup>13</sup> This is clearly seen from increase of the central C-N bond lengths and decrease of C=N bond lengths in the proton-transferred form. That is, while in CuN<sub>2</sub>O<sub>2</sub> chromophores the conjugation of  $\pi$  electrons is realized over the whole of the chelate rings, in CuN<sub>4</sub> chromophores with proton transfers the conjugation is separated at the central nitrogen. Stabilities of CuN2O2 chromophores relative to the CuN<sub>4</sub> chromophores are quite large (ca.  $15 \text{ kcal mol}^{-1}$ ). Given that deviations from planarity of each chelate ring in 6, 7, 10, and 11 are small, conformational energies of amide groups do not so much contribute to the total stabilities. Indeed, when torsion angles of the amide groups are less than 45°, the difference of conformational energies should be at most  $4-5 \text{ kcal mol}^{-1,21}$  In 6, the torsion angle of the trans-amide moiety is 15.7°, and in 10, the torsion angles of the cis-amide moieties are 32.1° (side-H-N-C-O) and 35.1° (central-H-N-C-O). Therefore, the large stabilities of CuN<sub>2</sub>O<sub>2</sub> chromophores are mainly attributed to the large delocalization energy in the chelate rings. In the carbamoyl  $-NH_2$  coordination 8 and 9, the delocalization energy is much



Figure 6. Optimized structures of bis(amidinourea)copper(II) ( $[AU - H]_2Cu$ ) at B3LYP/6-31G(d) level of theory. The parameters are units in Å and degrees.

 Table 1. Summary of DFT Calculations on Bis(amidinourea)copper(II) Isomers at B3LYP/6-31G(d)//B3LYP/6-31G(d) and B3LYP/

 6-31G(d,p)//B3LYP/6-31G(d,p) (in Parentheses)<sup>a)</sup>

Isoı	ners	Symmetry	Relative energy /kcal mol <sup>-1</sup>	ZPE <sup>d)</sup> /hartree (particle) <sup>-1</sup>	$\langle \boldsymbol{S}^2 \rangle^{\mathrm{e})}$
6	<i>trans</i> -CuN <sub>2</sub> O <sub>2</sub>	$C_2 = C_{2h}$	$0.0^{\rm b)} (0.0)^{\rm c)}$	0.187548	0.7521 <sup>b)</sup> (0.7521) <sup>c)</sup>
7	<i>cis</i> -CuN <sub>2</sub> O <sub>2</sub>	$C_2 = C_{2v}$	+4.1 (+2.2)	0.186799	0.7520 (0.7520)
8	trans-CuN <sub>4</sub>	$C_2$	+38.6(+39.1)	0.187308	0.7521 (0.7521)
9	cis-CuN <sub>4</sub>	$C_2$	+36.3(+37.0)	0.188186	0.7521 (0.7521)
10	<i>trans</i> -CuN <sub>4</sub> (Proton transferred)	$C_2$	+15.2(+14.6)	0.187700	0.7523 (0.7523)
11	cis-CuN <sub>4</sub> (Proton transferred)	$C_2$	+17.0 (+16.4)	0.187583	0.7523 (0.7523)

a) We note that symmetry classification  $C_2$  of **6** and **7** can be approximately regarded as  $C_{2h}$  and  $C_{2v}$ , respectively, due to the nearly planar geometries. b) B3LYP/6-31G(d)//B3LYP/6-31G(d), the same hereinafter. The total energy of **6** is -2387.359505 hartree. c) B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p), the same hereinafter. The total energy of **6** is -2387.393622 hartree. d) Zero-point energy at B3LYP/6-31G(d)//B3LYP/6-31G(d). e) Spin-squared expectation value before annihilation. Since  $\langle S^2 \rangle$  for a pure doublet state should be 0.7500, all the values suggest nearly exact doublet states.

reduced due to the nonplanarity of  $sp^3$ -like configuration. Indeed, these nonplaner geometries are reflected in the large instability in energy (over ca.  $35 \text{ kcal mol}^{-1}$ ). Thus, we can plausibly conclude that the lavender complex is a *trans* chelate compound **6** depicted in the top of Figure 6. A summary of the quantum-chemical calculations are shown in Table 1.

The frontier orbitals of neutral AU (1), AU anion  $([AU - H]^-)$ , and its *trans*-CuN<sub>2</sub>O<sub>2</sub> complex  $[AU - H]_2$ Cu are shown in Figures 7a, 7b, and 7c, respectively. AU has nearly nonbonding frontier  $\pi$  orbitals due to the bipartite skeleton, similar to odd alternant hydrocarbons. In addition, there are lone pairs on the carbonyl oxygen and the central

nitrogen. In the B3LYP/6-31G(d) level of theory, HOMO is the lone-pair orbital, and HOMO–1, HOMO–2, LUMO are characterized as  $\pi$ ,  $\pi$ , and  $\pi^*$  orbitals, respectively (Figure 7a). We see that the Schiff-base moiety has a weak bonding amplitude pattern, which is reflected in the  $\pi$ - $\pi^*$  UV absorption above and weak bond alternation of AU.<sup>9</sup> AU anion also has non-bonding HOMO and lone-pair orbitals (Figure 7b). The eigenvalues of frontier orbitals are much higher than those of neutral AU due to the anionic character. In particular, HOMO–1 and HOMO–2 are characterized as lone-pair orbitals of imino nitrogen and carbonyl oxygen, which serve as strong donor sites. The amplitudes at the amino groups are



Figure 7. Selected molecular orbitals of AU, deprotonated AU ( $[AU - H]^-$ ), and bis(amidinourea)copper(II) chelates ( $[AU - H]_2Cu$ ) at B3LYP/6-31G(d) level of theory. The eigenvalues of Kohn–Sham orbitals are unit in hartree.

relatively small. The frontier orbitals of the trans-CuN<sub>2</sub>O<sub>2</sub> complex consist of d orbital of Cu<sup>2+</sup> and the nonbonding fragments of AU (Figure 7c). The singly occupied molecular orbital (SOMO) consists of antibonding interactions between the  $d_{xv}$  component and lone pairs of the carbonyl oxygens and imino nitrogens. The amplitudes on the remaining nitrogens are also not trivial. Therefore, ESR hyperfine structures reported by early workers<sup>8</sup> are attributed to not CuN<sub>4</sub> chromophores, but the nitrogen atoms in the trans-CuN<sub>2</sub>O<sub>2</sub> chromophore and the second nearest-neighbor nitrogens, contrary to bis(biguanide)copper(II),<sup>22</sup> bis(O-alkylamidinourea)copper(II).<sup>23,24</sup> The other occupied frontier orbitals also come from the d components and nonbonding moieties of AU. However, nonplanarity of the complex allows them to interact with each other to afford  $\pi$ - $\sigma$ mixed orbitals. The vis spectra are attributed to the transition from these  $\pi$ - $\sigma$  mixed orbitals to SOMO. Indeed, TDDFT (time-dependent DFT) calculations at the same level predicted the transition from the  $\pi$ - $\sigma$  mixed orbitals (for example, SOMO-2) to SOMO with 552.9 nm, which is nearly consistent with the experimental data. It is noteworthy that the absorption coefficients (obs.  $\varepsilon = 40$ ) in visible region is relatively smaller than those of general Schiff-base complexes.<sup>25</sup>

All the optimized structures of the *trans*- and *cis*-chelates belong to  $C_2$  point group, as discussed above. However, if the degree of nonplanarity is small, the *trans*-chelates are regarded as  $C_{2h}$  molecules with an inversion center, and *cis*-chelates are regarded as  $C_{2v}$  molecules. Therefore, we can expect the mutual exclusion rule for IR/Raman spectra for the most stable *trans*isomer. Figure 8 shows IR/Raman spectra of the complex within 1800–700 cm<sup>-1</sup> and the corresponding calculated data. IR and Raman peaks are approximately classified into antisymmetric and symmetric modes with respect to the copper atom, respectively. In particular, large peaks (for example, ring-breathing at 952 and 956 cm<sup>-1</sup>) approximately satisfies the mutual exclusion rule, in which IR and Raman peaks do not coexist at the same wavenumber. In the fingerprint region (below  $1300 \,\mathrm{cm}^{-1}$ ), we see good consistency between the observed and calculated profiles within the scale factor errors (0.96 for B3LYP/6-31(d)).<sup>26</sup> NH<sub>2</sub> rocking peaks around 1132 and 1134 cm<sup>-1</sup> are probably coupled between the adjacent modes, and the order of the wavenumber is slightly changed in the observed data. Above 1300 cm<sup>-1</sup>, deviations from theoretical are slightly large due to perturbation of molecular fields. For example,  $NH_2$  scissoring peaks 1469 and 1474 cm<sup>-1</sup> (calcd.) are considerably shifted to low-energy due to the edge effects. Nevertheless, as a whole, most of the peaks were reasonably assigned. The local molecular fields are probably asymmetric to violate the selection rule to some extent, and the IR/Raman intensities slightly deviate from theoretical prediction. As for the high wavenumber region, each peak is subject to molecular fields grossly, because the vibrations are localized at specific functional groups or terminal residues. Thus, the vibrations do not so much interact all over the molecule, and the mutual exclusion rule is also not so important. However, we emphasize the remarkable IR-band shift of the nonassociated carbonyl stretching: before coordination, obs.  $1734 \text{ cm}^{-1}$ ,<sup>11</sup> calcd.  $1719 \text{ cm}^{-1}$ ; after coordination, obs.  $1622 \text{ cm}^{-1}$ , calcd. 1643 cm<sup>-1</sup>. For reference, the details of IR/Raman simulations of  $[AU - H]_2Cu$  for all the wavenumbers are summarized in the Supporting Information.

Remarkable data associated with the metal–ligand bonds appeared below 700 cm<sup>-1</sup>. Figure 9 shows comparison of IR



**Figure 8.** Experimental and theoretical IR/Raman spectra of bis(amidinourea)copper(II) ( $[AU - H]_2Cu$ ) at 1800–700 cm<sup>-1</sup>. Each approximate assignment corresponds to the pair of antisymmetric/symmetric (IR/Raman) modes. The Raman peak 1648 cm<sup>-1</sup> (calcd.) is –NH<sub>2</sub> scissoring rather than C=O stretching. Notation:  $\omega$ ; wagging,  $\tau$ ; twisting,  $\rho$ ; rocking,  $\sigma$ ; scissoring,  $\nu$ ; stretching.

and Raman spectra of the complex within 700–400 cm<sup>-1</sup>. We see that the wavenumber of each Raman peak never coincides with that of the IR peak. That is, the exclusion rule for IR/ Raman intensities exactly holds. In particular, symmetric and antisymmetric Cu–O (partially containing Cu–N) stretching modes  $\nu_{\rm s}$  (Cu–O) and  $\nu_{\rm as}$  (Cu–O) are clearly separated into Raman and IR activities, respectively. This suggests that the complex is the *trans*-isomer with an inversion center.

Figure 10 shows schematic representation of the symmetric and antisymmetric Cu–O stretching modes obtained by the vibration analysis. The observed wavenumbers corresponding to these stretching modes are very close to those of typical complexes bis(glicinate)Cu(II)<sup>27</sup> or tetraamminecobalt(III) salts.<sup>28</sup> In particular, our results are comparable to  $\nu_{as}$  and  $\nu_{s}$  in *trans*-bis(glicinate)Cu(II)·2H<sub>2</sub>O:<sup>27</sup> IR; 483 cm<sup>-1</sup> ( $\nu_{as}$ ), Raman; 462 cm<sup>-1</sup> ( $\nu_{s}$ ) (Though the approximate assignment in the original paper is Cu–N,<sup>27</sup> these are probably coupled with Cu–O to a large extent.). Table 2 shows a summary of the IR/Raman spectra at 700–400 cm<sup>-1</sup>. The DFT-calculated data (B3LYP/



Figure 9. Mutual exclusion rule for IR/Raman spectra of bis(amidinourea)copper(II) ( $[AU - H]_2Cu$ ) at 700–400 cm<sup>-1</sup>.



**Figure 10.** Symmetric and antisymmetric Cu–O (Cu–N) stretching modes of bis(amidinourea)copper(II) ([AU – H]<sub>2</sub>Cu).

6-31G(d)) are also shown. All the observed peaks were well reproduced and attributed as stretching or bending modes. Though we can use the scaling factor for B3LYP calculations if necessary, the present simulation is quite adequate for assignment of each peak.

## **Theoretical Aspects of the Electronic States**

Quasi Aromaticity in Anionic Amidinourea–Cu(II) Complexes. The origin of stability of the  $CuN_2O_2$  chromophore is not so evident from DFT calculations only. Given that the amino-coordinated complexes are evidently eliminated as above, we here focus on the energetics of *trans*-CuN<sub>2</sub>O<sub>2</sub> (6) and proton-transferred *trans*-CuN<sub>4</sub> (10) chelates. From the viewpoint of valence bond (VB) descriptions, the CuN<sub>2</sub>O<sub>2</sub> chelate

Table 2. Summary of IR and Raman Spectra at 700– $400 \text{ cm}^{-1}$ 

Observed /cm <sup>-1</sup>	Calculated <sup>a),b)</sup> /cm <sup>-1</sup>	Assignment	Notation <sup>c)</sup>	
IR				
418	421	–NH <sub>2</sub> wagging	$\omega$ (NH <sub>2</sub> )	
457	471	-NH <sub>2</sub> rocking	$\rho$ (NH <sub>2</sub> )	
496	507	Cu-O stretching,	$\nu_{as}$ (Cu–O)	
		antisymmetric		
513	542	–NH <sub>2</sub> twisting	$\tau$ (NH <sub>2</sub> )	
528	553	-NH <sub>2</sub> wagging	$\omega$ (NH <sub>2</sub> )	
634	638	>N-H rocking	$\rho$ (NH)	
690	669	>N-H wagging	$\omega$ (NH)	
706	689	>N–H wagging	$\omega$ (NH)	
Raman				
478	471	-NH <sub>2</sub> rocking	$\rho$ (NH <sub>2</sub> )	
482	502	Cu-O stretching,	ν <sub>s</sub> (Cu–O)	
		symmetric		
ca. 505 <sup>d)</sup>	539	–NH <sub>2</sub> twisting	$\tau$ (NH <sub>2</sub> )	
520	552	-NH <sub>2</sub> wagging	$\omega$ (NH <sub>2</sub> )	
665	638	>N-H rocking	$\rho$ (NH)	
ca. 690?	669	>N-H wagging	$\omega$ (NH)	
695	693	>N-H wagging	$\omega$ (NH)	

a) Calculated under B3LYP/6-31G(d) level of theory. No scaling factors are used. b) Calcd. 638 and  $669 \text{ cm}^{-1}$  are very weak, and not completely mutual-excluded due to the deviation of symmetry. c) Corresponding to Figure 9. d) Shoulder.

ring has  $6\pi$  electrons, and the proton-transferred CuN<sub>4</sub> chelate ring has  $7\pi$  electrons. Two fragments of chelate rings bind through Cu(II) to form  $20\pi$  electron systems. Figure 11 shows one of the representative resonance structures for the CuN<sub>2</sub>O<sub>2</sub> (for 6) and  $CuN_4$  (for 10) chelate rings. In the  $CuN_4$  chelate rings, all the coordinated nitrogens are imino type. Each ligand with  $10\pi$  electrons is approximately described by Hückel molecular orbitals of tetramethylenepropane trianion (TMP<sup>3-</sup>). In view of molecular orbital (MO) theory,  $6\pi$  systems form a bonding "shell" under the nonbonding levels, and each branched amino nitrogen has lone-pair electrons due to the nonbonding levels. In  $7\pi$  systems, on the other hand,  $\pi$ -electron densities on the branched carbonyl oxygens will become close to unity. If  $\pi$ -electrons on Cu are nontrivial, the  $6\pi$  systems are thought to be much stable than  $7\pi$  systems due to quasi aromaticity. In the meantime, we use the term "quasi aromaticity" for describing apparently cyclic compounds of which the most plausible resonance structure contains  $(4n + 2)\pi$ electrons in the ring moieties. Theoretically speaking, quasi aromaticity is rationalized by Gimarc's topological charge stabilization rule;29-32 electronegativities of the constituent atoms match the pattern of electron density distribution of the isoelectronic hydrocarbon. However, as shown below, the present  $6\pi$ - $7\pi$  energetics is concisely solved by perturbation theory.

Given that the unpaired electron on SOMO has  $\sigma$  character, we separate it from the present analysis. Mulliken population of the DFT results shows that  $4p_z$  orbital of Cu participates in forming the frontier orbitals to an extent, in which magnitude of the amplitude is ca. 0.1-0.2. The nontrivial coefficients result from the residual 4p component after the dsp<sup>2</sup> hybridization. The HOMOs of TMP<sup>3-</sup> are shown in the middle of Figure 11. These are triply degenerate nonbonding molecular orbitals (NBMOs),<sup>33</sup> in which the amplitudes of branched methylene groups are relatively large. 6 and 10 consists of two TMP<sup>3-</sup> fragments and Cu(II), and their MOs are also approximately constructed by the Hückel method with heteroatom parameters. Now, we consider an isoelectronic hydrocarbon corresponding to the complexes as the zero-th order approximation. The skeleton is shown in Figure 11. We note that the central site is formally linked to the four adjacent sites. This is a hypothetical pentaanion of which NBMOs are fivefold degenerate. The MO levels of the isoelectronic hydrocarbon with  $20\pi$  electrons are also shown in Figure 11. Let us consider change of the Coulomb integrals to evaluate the energy of 6and 10. The energy change is estimated by the perturbation theory without ab initio calculations. Change of  $\sigma$ -bond energy is trivial, because the tautomerism is formally regarded as proton transfer between two lone pairs on the same pyridinetype nitrogen atoms. Within the second-order perturbation, the change of the Coulomb integrals  $\delta \alpha_r$  (in unit of the standard resonance integral  $\beta$ ) on the *r*-th site is reflected in the total energy E.34

$$E \cong E_0 + \sum_r q_r \delta \alpha_r + \sum_r \frac{1}{2} \pi_{r,r} (\delta \alpha_r)^2 + \sum_{r,s} \delta E_{\text{bond}} (\delta \beta_{r,s})$$
(1)

 $E_0$  is the  $\pi$ -electron energy of the reference hydrocarbon.  $\delta E_{\text{bond}}(\delta \beta_{r,s})$  is energy change by deviation  $\delta \beta_{r,s}$  from the resonance integral  $\beta$ . However, this term is small, and almost cancelled out when only energy difference between the two isomers is sought.  $q_r$  is  $\pi$  electron density on the *r*-the site, and  $\pi_{r,r}$  is self-atom polarizability in the reference hydrocarbon:

$$\pi_{r,r} = 4 \sum_{j}^{\text{occ}} \sum_{k}^{\text{unocc}} \frac{C_{jr}^2 C_{kr}^2}{\varepsilon_j - \varepsilon_k}$$
$$\cong 4 \sum_{j}^{\text{NBMOs}} \sum_{k}^{\text{LUMOs}} \frac{C_{jr}^2 C_{kr}^2}{\varepsilon_{\text{NBMO}} - \varepsilon_{\text{LUMO}}}$$
(2)

where  $C_{jr}$  is the coefficients of the *j*-th Hückel MO on the *r*-th site. Within the first-order perturbation, the gap  $E(\text{CuN}_4) - E(\text{CuN}_2\text{O}_2)$  is too roughly estimated. Through the second-order perturbation, many components of the excited configurations are mixed, and the estimation is highly improved. Then, only NBMO–LUMO interactions are important for our purpose, because they mainly contribute to eq 2. The  $\pi$ -electron density  $q_r$  of the reference hydrocarbon is shown in Figure 11. Supposing that  $\delta \alpha_r(\text{amino N}) = 1.5\beta$ ,  $\delta \alpha_r(\text{carbonyl O}) = 1.0\beta$ ,  $\delta \alpha_r(\text{imino N}) = 0.5\beta$ , and the resonance integral for benzenoids  $\beta = -1.0 \text{ eV}$ ,<sup>34</sup>

$$E(\operatorname{CuN}_4) - E(\operatorname{CuN}_2O_2)$$
  
= 0.208|\beta| (1st order) + 0.184|\beta| (2nd order)  
\approx 9.0 kcal mol^{-1} (3)

The order of the energy difference is consistent with the DFT results. Magnitude of the Coulomb integral on Cu(II) is probably half as large as that of carbon. However, this is not



Figure 11. Construction of molecular orbitals of bis(amidinourea)metal(II). Dots in the molecular structures represent  $\pi$  electrons. The isoelectronic hydrocarbon for the ligand is tetramethylenepropane trianion (TMP<sup>3-</sup>), of which NBMOs are threefold degenerate. Isoelectronic hydrocarbon for the complex has fivefold degenerate NBMOs. The numerals on the skeleton of the complex are the  $\pi$ -electron densities  $q_r$  and approximate self-atom polarizabilites  $\pi_{r,r}$  (in parentheses, unit in  $\beta^{-1}$ ).

necessary explicitly due to cancelation. It is essential that  $q_r$ and  $\delta \alpha_r$  of the branched amino group are relatively significant, and thus, contribution to the first-order stability becomes large. This situation corresponds to the conventional topological charge stabilization rule. The absolute value of self-atom polarizabilities  $\pi_{r,r}$  on the branched positions also becomes large due to significant NBMO amplitudes on the branched positions. This contributes to the second-order perturbation, and stabilizes the CuN<sub>2</sub>O<sub>2</sub> chromophore with significant  $\delta \alpha_r$  of amino groups. This implies that the topological charge stabilization rule can be modified by the second-order perturbation. The applicability of the extended rule to other systems will be discussed elsewhere by further studies on other quasi-aromatic molecules. Thus, as a whole, we can plausibly conclude that the bis(amidinourea)copper(II) formed under basic conditions has a trans-CuN<sub>2</sub>O<sub>2</sub> chromophore, not CuN<sub>4</sub> chromophores.

Systematic Calculations on Other Metal's Complexes. Amidinourea anion forms complexes with various metals. However, there are few structural studies except for early speculations. Let us consider complexes of Ni(II), Pd(II), Zn(II), and Cd(II) as comparative examples of Cu(II). The Ni(II) complexes are known as orange materials, of which structures have been speculated to have CuN4 chromophores assuming uncertain tautomerism.<sup>1</sup> The Pd(II) complexes are also reported in the early literature as light yellow materials,<sup>1</sup> but the structures are unknown. Zn(II) complexes are known as white powder with some crystal waters,<sup>1</sup> though the structures are unknown. A Cd(II) complex is known as white powder.<sup>2</sup> Cd(II) is weakly adsorbed by methacryloyl AU resins in basic solutions,<sup>12</sup> which suggests similar chelation. The Cd(II) complexes are of interest in view of environmental chemistry, but the structure is also unknown. Though Zn(II) and Cd(II) are not

Metal M(II)	Isomers	Symmetry	Charge on M	Tilt angle /degree	Relative energy /kcal mol <sup>-1</sup>	$\langle \boldsymbol{S}^2 \rangle^{\mathrm{a})}$	
Cu(II) 6	<i>trans</i> -CuN <sub>2</sub> O <sub>2</sub>	$C_2 = C_{2h}$	+0.840(+0.836)	28.3 (34.4)	0.0 (0.0)	0.7521 (0.7521)	
Cu(II) 10	trans-CuN <sub>4</sub> (Proton transferred)	$C_2$	+0.811 (+0.802)	44.2 (40.6)	+15.2 (+14.6)	0.7523 (0.7523)	
		[B3LYP/6-31G(d)//B3LYP/6-31G(d) (in parentheses, B3LYP/6-31G(d,p)// B3LYP/6-31G(d,p))]					
Ni(II)	trans-CuN <sub>2</sub> O <sub>2</sub>	$C_2 = C_{2h}$	+0.725(+0.723)	2.8 (2.7)	0.0 (0.0)	0.0000 (0.0000)	
Ni(II)	<i>trans</i> -CuN <sub>4</sub> (Proton transferred)	$C_2 = C_{2h}$	+0.718(+0.712)	9.8 (10.1)	+14.6(+14.1)	0.0000 (0.0000)	
[B3LYP/6-31G(d)//B3LYP/6-31G(d) (in parentheses, B3LYP/6-31G(d,p)// B3LYP/6-31G(d,p))]							
Pd(II)	trans-CuN <sub>2</sub> O <sub>2</sub>	$C_2 = C_{2h}$	+0.520	0.63	0.0	0.0000	
Pd(II)	<i>trans</i> -CuN <sub>4</sub> (Proton transferred)	$C_2 = C_{2h}$	+0.567	1.21	+8.3	0.0000	
		[B3LYP/LANL2DZ//B3LYP/LANL2DZ]					
Zn(II)	trans-CuN <sub>2</sub> O <sub>2</sub>	$C_2$	+0.938(+0.933)	87.4 (87.4)	0.0 (0.0)	0.0000 (0.0000)	
Zn(II)	trans-CuN <sub>4</sub> (Proton transferred)	$C_2$	+0.885(+0.875)	85.3 (85.3)	+15.1(+14.5)	0.0000 (0.0000)	
		[B3LYP/6-31G(d)//B3LYP/6-31G(d) (in parentheses, B3LYP/6-31G(d,p)// B3LYP/6-31G(d,p))]					
Cd(II)	trans-CuN <sub>2</sub> O <sub>2</sub>	$C_2$	+1.072	85.1	0.0	0.0000	
Cd(II)	<i>trans</i> -CuN <sub>4</sub> (Proton transferred)	$C_2$	+1.027	83.3	+20.7	0.0000	
[B3LYP/LANL2DZ//B3LYP/LANL2DZ]							

Table 3. Summary of DFT Calculations on Bis(amidinourea)metal(II) Isomers

a) The Ni(II) and Pd(II) complexes are thought to be diamagnetic.<sup>1,8</sup>

transition metals, their chelates are interesting as comparative examples with the Cu(II) complex.

If quasi aromaticity plays a dominant role in the tautomerism, these complexes should also have stable CuN<sub>2</sub>O<sub>2</sub> chromophores. Thus, our interest is geometries and the relative energies of the metal (M)-N<sub>2</sub>O<sub>2</sub> and M-N<sub>4</sub> chromophores. Table 3 is the summary of the calculations. We see that trans-MN<sub>2</sub>O<sub>2</sub> isomers are stable for all the metal ions. The tilt angle between the two chelate planes suggests dsp<sup>2</sup> hybridization for Ni(II) and Pd(II) complexes, and sp<sup>3</sup> hybridization for Zn(II) and Cd(II) complexes. In the actual computations, LANL2DZ basis set was used for Pd and Cd atoms. Then, valence of Cd(II) is described by sd<sup>3</sup> hybridization using 5d atomic orbital components, rather than sp<sup>3</sup> hybridization. In Ni(II) and Pd(II) complexes, we can expect large quasi-aromaticity effects, because deviation from planarity is very small. Then, the vacant  $4p_z$  and  $5p_z$  atomic orbitals are responsible for  $\pi$  conjugations in the Ni(II) and Pd(II) complexes, respectively. The mechanism of the quasi-aromaticity stabilities of these complexes is similar to that of Cu(II) (eq 3).

In the Zn(II) and Cd(II) complexes, on the other hand, quasi aromaticity is realized by hyperconjugation of  $\sigma_{\pi}$  orbitals consisting of sp<sup>3</sup> or sd<sup>3</sup> components. The  $\sigma_{\pi}$  orbitals have  $\pi$ symmetry, as depicted in the bottom of Figure 11, and conjugates with the ligands. This kind of interaction is similar to those of alkyl benzenes or polyphenols, in which  $\sigma_{\pi}$  orbitals consisting of sp<sup>3</sup> orbitals on carbon and 1s on hydrogen participate in hyperconjugation.<sup>35</sup> In general, whether a given  $\pi$  system is stabilized or destabilized by hyperconjugation depends on the situation. In the present cases, the interactions always stabilize the nonperturbed structures, because the active orbitals on metal ions are vacant. In the cases of Zn(II) and Cd(II), the choice of the zero-th order structures is different from those of the Cu(II), Ni(II), and Pd(II) complexes. Given that charges on the Zn(II) and Cd(II) are larger than those of the Cu(II), Ni(II), and Pd(II) complexes (Table 3), two perpendicularly twisted resonance structures with the metal's vacant  $\sigma_{\pi}$  orbitals and NBMOs of TMP<sup>3-</sup> are probably suitable for the nonperturbed structures. Then, the total energies of these complexes are similarly calculated as:

$$E(MN_4) - E(MN_2O_2)$$
  
= 0.250|\beta| (1st order) + 0.442|\beta| (2nd order)  
\approx 16.0 kcal mol^{-1} (M = Zn and Cd) (4)

Within the first-order perturbation, the branched amino groups stabilize the system to a large extent, because  $q_r$  on branched carbons are relatively large and  $\delta \alpha_r$  of amino nitrogen is also significant. In addition, it can be easily shown that selfatom polarizability on the central carbon of the TMP<sup>3-</sup> is smaller than those of the branched positions, because the coefficient in the LUMO is zero. Therefore, the second-order perturbation mainly comes from self-atom polarizabilities on the branched positions. Given that  $\delta \alpha_r$  of amino nitrogen is more significant than those of inimo nitrogen or oxygen, contributions to the first- and second-order perturbation stability is mainly due to branching of the amino groups. Thus, we can conclude that branching of amino groups is more preferable than those of imino groups or carbonyl oxygen. This is the essential origin of MN<sub>2</sub>O<sub>2</sub> preference.

As a whole, discussions by the perturbation theory above are fully consistent with the experiments and DFT results, and magnitude of the stability of *trans*-MN<sub>2</sub>O<sub>2</sub> chromophores is robust. From the estimated energy gaps between the MN<sub>2</sub>O<sub>2</sub> and MN<sub>4</sub> chromophores, the equilibrium constants [MN<sub>4</sub>]/ [MN<sub>2</sub>O<sub>2</sub>] becomes less than 10<sup>-6</sup> (in particular, 10<sup>-15</sup> order for M = Cu) at room temperature. The thermal stability of the *trans*-isomer relative to the *cis*-form is estimated to be ca. 4 kcal mol<sup>-1</sup>, which is large enough to separate it at room temperature. The experimental and theoretical results are fully consistent. Thus, stability of the  $CuN_4$  chromophores that have been supported by early studies is very suspicious. Despite many studies, the single crystals of  $[AU - H]_2Cu$  and the related compounds have not been obtained yet at present. However, complexes of substituted AUs, say, long-alkyl AUs, may be crystallized from usual solvents more easily. It is to be desired that crystallographic studies are performed in the future by specialists of X-ray or neutron-diffraction analyses to establish the MN<sub>2</sub>O<sub>2</sub>–MN<sub>4</sub> energetics.

#### Conclusion

Coordination structures of bis(amidinourea)copper(II) chelates were suggested by substituent effects of complexation, UV–vis spectra, IR/Raman spectra, and DFT analysis. Contrary to early speculations, the anionic amidinourea–Cu(II) complex plausibly has a *trans*-CuN<sub>2</sub>O<sub>2</sub> chromophore, not CuN<sub>4</sub> chromophores. DFT calculations revealed relative stabilities of the possible isomers. Vibration analysis and the exclusion rule for IR/Raman spectra were consistent with the *trans*-CuN<sub>2</sub>O<sub>2</sub> preference. Systematic DFT calculations on bis(amidinourea)– Cu(II), –Ni(II), –Pd(II), –Zn(II), and –Cd(II) also supported the metal–N<sub>2</sub>O<sub>2</sub> preference, and the essential origin of the stability was clarified by the perturbation theory. The branched amino groups contribute to the metal–N<sub>2</sub>O<sub>2</sub> preference to a large extent through the topological charge stabilization.

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## **Supporting Information**

For the bis(amidinourea)copper(II) complexes, fully optimized Cartesian coordinates, details of the energetics, and IR/ Raman simulation results. This material is available electronically on J-STAGE.

## References

- 1 P. Rây, Chem. Rev. 1961, 61, 313.
- 2 R. H. Trimble, Anal. Chem. 1962, 34, 1633.
- 3 C. R. Saha, D. Sen, S. Guha, J. Chem. Soc., Dalton Trans. 1975, 1701.
- 4 P. V. Babykutty, C. P. Prabhakaran, R. Anantaraman, C. G. R. Nair, J. Inorg. Nucl. Chem. 1977, 39, 913.
- 5 A. Syamal, Indian J. Chem., Sect. A: Inorg., Phys., Theor. Anal. 1985, 24, 946.

6 M. J. Begley, P. Hubberstey, C. H. M. Moore, J. Chem. Res., Synop. 1986, 120.

7 M. J. Begley, P. Hubberstey, S. P. Martindale, C. H. M. Moore, N. S. Price, *J. Chem. Res., Synop.* **1988**, 2.

8 R. K. Ray, G. B. Kauffman, *Inorg. Chim. Acta* 1990, 173, 207.

9 M. J. Begley, P. Hubberstey, C. H. M. Moore, J. Chem.

Res., Synop. 1985, 380.

10 A. W. Trochimczuk, B. N. Kolarz, *Eur. Polym. J.* **2000**, *36*, 2359.

11 a) M. Hatanaka, M. Hoshi, R. Shiba, *Kobunshi Ronbunshu* **2006**, *63*, 745. b) M. Hatanaka, *Non-bonding properties of ureas* in *Urea: Synthesis, Properties and Uses*, ed. by C. M. Muñoz, A. M. Fernández, Nova Science Publishers, **2012**, New York, Chap. 8, pp. 213–231.

12 S. Tanaka, M. Hatanaka, T. Shimizu, R. Shiba, *Kobunshi Ronbunshu* **2009**, *66*, 43.

- 13 R. C. Hirt, R. G. Schmitt, Spectrochim. Acta 1958, 12, 127.
- 14 C. Lee, W. Yang, R. G. Parr, Phys. Rev. B 1988, 37, 785.
- 15 A. D. Becke, J. Chem. Phys. 1993, 98, 1372.
- 16 A. D. Becke, J. Chem. Phys. 1993, 98, 5648.

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, 17 M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, N. Rega, P. Salvador, J. J. Dannenberg, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian 98 (Revision A.11.2), Gaussian, Inc., Pittsburgh PA, 2001.

18 T. Ebisuno, M. Takimoto, M. Takahashi, R. Shiba, *Bull. Chem. Soc. Jpn.* **1989**, *62*, 651.

- 19 Z. B. Maksić, B. Kovačević, J. Org. Chem. 2000, 65, 3303.
- 20 M. Hatanaka, Comput. Theor. Chem. 2011, 971, 58.
- 21 S. Ilieva, B. Hadjieva, B. Galabov, J. Mol. Struct. 1999, 476, 151.
- 22 R. K. Ray, G. B. Kauffman, *Inorg. Chim. Acta* **1990**, *174*, 237.
- 23 J. R. Wasson, C. Trapp, J. Phys. Chem. 1969, 73, 3763.
- 24 O. I. Singh, M. Damayanti, N. R. Singh, R. K. H. Singh, M. Mohapatra, R. M. Kadam, *Polyhedron* **2005**, *24*, 909.
- 25 H. Ünver, A. Elmali, A. Karakaş, H. Kara, E. Donmez, *J. Mol. Struct.* **2006**, *800*, 18.
  - 26 M. W. Wong, Chem. Phys. Lett. 1996, 256, 391.
- 27 J. R. Kincaid, K. Nakamoto, *Specrtochim. Acta, Part A* **1976**, *32*, 277.
- 28 K. Kanamori, K. Kawai, Bull. Chem. Soc. Jpn. 1982, 55, 764.
  - 29 B. M. Gimarc, J. Am. Chem. Soc. 1983, 105, 1979.
- 30 B. M. Gimarc, J. J. Ott, J. Am. Chem. Soc. 1986, 108, 4298.
- 31 J. J. Ott, B. M. Gimarc, J. Am. Chem. Soc. 1986, 108, 4303.
- 32 J. Aihara, Bull. Chem. Soc. Jpn. 1987, 60, 2268.

33 M. Hatanaka, R. Shiba, J. Comput. Chem., Jpn. 2005, 4, 101.

34 A. Streitwieser, Jr., *Molecular Orbital Theory for Organic Chemists*, John Wiley & Sons, New York, **1961**.

35 M. Hatanaka, Tetrahedron Lett. 2013, 54, 1452.