Structural and Electronic Effects on the 
Polarographic Half-Wave Potentials of 
Copper (II) Chelate Complexes

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ABSTRACT

Polarographic measurements in dimethylformamide solution have been 
performed on 37 bis-chelate Cu(II) complexes containing primarily salicyl- 
laidimine, β-ketoamine, β-iminoamine, and pyrrole-2-aldimine ligand systems. 
The complexes were selected in order to reveal the effect of stereochemical 
and donor atom variations on half-wave potentials. Mono- and binuclear 
complexes undergo one- and two-electron reductions, respectively, which were 
established for representative cases by controlled potential coulometry. The 
response of Cu(II)/Cu(I) potentials to these variations reveals that nonplanar 
bis-chelate complexes are easier to reduce than their planar analogs, rigid 
planar tetradentate or related planar bis-chelate complexes, and complexes 
differing only in donor atoms are more readily reduced in the order N<sub>4</sub> < 
N<sub>2</sub>O<sub>2</sub> < N<sub>2</sub>S<sub>2</sub>. Binuclear complexes are reduced in one two-electron or two 
resolvable one-electron steps depending on ligand structure. Potentials of these 
and other complexes previously examined are considered in relation to the 
markedly positive potentials of "blue" copper proteins and ligand structural 
features which might afford Cu(II)/Cu(I) potentials in the protein range are 
noted.

INTRODUCTION

Among the distinctive features of "blue" copper sites in proteins and enzymes 
[1-3] are markedly positive Cu(II)/Cu(I) redox potentials (ca. +0.2 to +0.8 V 
[1,2,4-8] at pH~7 vs the standard hydrogen electrode), indicating a more 
effective stabilization of Cu(I) vs Cu(II) than is usually the case for complexes of 
synthetic origin (vide infra). In the absence of high resolution X-ray diffraction 
information, the composition and geometry of these sites are unknown. However, 
the presence of a cysteinyl residue appears necessary for the occurrence of "blue" copper 
[9-12] with some or all of the remaining 
coordination positions possibly occupied by nitrogen ligands [13] in coordi-
nation units of tetrogonal or lower [14,15] ligand field symmetry. Possible 
geometries such as five-coordinate or pseudotetrahedral are difficult to dis-
tinguish because of their low symmetry and the viability of the latter has been considered in some detail [1-3,16]. Evidence for a nonplanar, possibly four-coordinate site with one sulfur ligand for "blue" copper is indirect at best. This or any other description of the coordination unit and its protein environment must ultimately be reconcilable with the relatively positive redox potentials, which reach a maximum with Polyporus laccase ($E^\circ_0 = +0.77$ V$^1$; compare $E^\circ_0 = +0.17$ V for aqueous Cu$^{2+/+}$).

The origin of the high protein potentials is a well recognized problem [1,2,17]. Previous qualitative considerations [17,18] together with potentials for complexes in aqueous solution [17,19,20] reveal that reduction potentials can be shifted to more positive values by the use of ligands which sterically or electronically destabilize tetragonal Cu(II) and/or enhance the stabilization of (presumably tetrahedral) Cu(I). In devising models of the "blue" copper sites or, possibly, in interpreting protein potentials, it could be advantageous to have knowledge of the sensitivity of Cu(II)/Cu(I) potentials to controlled structural and ligand electronic variations, even if the complexes are derived from nonphysiological ligands and their potentials do not occur in the protein range. Existing redox data on copper complexes, while extensive, are not well-suited to disclosure of such effects due to differences in methods of potential measurements, reference electrodes, solvent, pH, ligand systems, and, in nearly all cases, the lack of definite structural information for the oxidized and reduced forms.

In this investigation, a systematic study of polarographically determined Cu(II)/Cu(I) potentials has been undertaken utilizing series of complexes selected to reveal the effects of stereochemistry of one or both oxidation states and, to a lesser extent, ligand electronic properties on the values of these potentials. The complexes examined are represented in Fig. 1 and are listed in Table 1 together with their abbreviated names. They are not intended as models for ligation of "blue" copper inasmuch as the ligands employed are obviously of a nonphysiological nature. Except for 35-37 the ligands are of the essential Schiff base type, the principal advantage of which is the ability to vary stereochemistry by alteration of N-substituents. As will become evident, the potentials for these complexes do not fall in the protein range. Rather, it is changes in potentials relative to specified reference complexes which provide the more useful information.

**EXPERIMENTAL SECTION**

**Preparation of compounds**

The following complexes (cf. Table 1) were synthesized by published methods: 1, 2 [22]; 3, 4 [23]; 5, 6 [24]; 7, 8 [25]; 14 [26]; 15, 16 [27]; 17-22 [28]; 23 [29]; 24, 25 [30]; 28, 29 [31]; 30 [32]; 31 [26]; 32 [33]; 33 [34]; 34 [26]; 35 [35]; 36, 37 [36].
FIG. 1. Numbers and structural formulas of Cu(II) complexes.
<table>
<thead>
<tr>
<th>No.</th>
<th>Compound Name</th>
<th>$E_{1/2}$</th>
<th>$V^d$</th>
<th>Slope</th>
<th>$n^d$</th>
<th>$\angle (deg)$</th>
<th>$\nu, \text{cm}^{-1} (\text{cm}^{-1})$</th>
<th>CHCl$_3$</th>
<th>DMF</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>Cu(Me-sal)$_2$</td>
<td>-0.90</td>
<td>69</td>
<td>-</td>
<td>$\sim 0^c$</td>
<td>17,200 (154)</td>
<td>17,500 (50)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Cu(En-sal)$_2$</td>
<td>-0.86</td>
<td>62</td>
<td>-</td>
<td>$9.4^d$, $36^e$</td>
<td>16,900 (127)</td>
<td>17,200 (109)</td>
<td></td>
<td></td>
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<tr>
<td>3</td>
<td>Cu(IP-sal)$_2$</td>
<td>-0.74</td>
<td>65</td>
<td>-</td>
<td>$60^f$</td>
<td>15,900 (138)</td>
<td>15,900 (140)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Cu(Bu-sal)$_2$</td>
<td>-0.68</td>
<td>56</td>
<td>-</td>
<td>$54^g$, $62^h$</td>
<td>12,800 (236)</td>
<td>12,200 (243)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Cu(sal)$_2$ eq</td>
<td>-1.21</td>
<td>48</td>
<td>0.94</td>
<td>-</td>
<td>17,800 (231)</td>
<td>17,900 (213)</td>
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<td></td>
</tr>
<tr>
<td>6</td>
<td>Cu(sal)$_2$ o-phen</td>
<td>-1.11</td>
<td>58</td>
<td>1.08</td>
<td>-</td>
<td>$\sim 17,500$ (350)</td>
<td>17,900 (485)</td>
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<td></td>
</tr>
<tr>
<td>7</td>
<td>Cu(sal)$_2$ bp</td>
<td>-0.75</td>
<td>56</td>
<td>1.03</td>
<td>37$^j$</td>
<td>$\sim 12,300$ (38)</td>
<td>11,800 (41)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Cu(sal)$_2$ bmp</td>
<td>-0.78</td>
<td>56</td>
<td>1.07</td>
<td>np</td>
<td>$\sim 12,000$ (57)</td>
<td></td>
<td></td>
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<tr>
<td>9</td>
<td>Cu(S-Bu-sal)$_2$ bmp</td>
<td>-0.83</td>
<td>57</td>
<td>-</td>
<td>np</td>
<td>$\sim 12,100$ (59)</td>
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<td></td>
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<tr>
<td>10</td>
<td>Cu(S-Bu-sal)$_2$ bp</td>
<td>-0.78</td>
<td>56</td>
<td>-</td>
<td>np</td>
<td>$\sim 15,900$ (49)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Cu$_2$ (sal)$_2$ (bp)</td>
<td>-0.71</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>$\sim 12,000$ (96)</td>
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<td></td>
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<tr>
<td>12</td>
<td>Cu$_2$ (S-Bu-sal)$_2$ (m-phen)$_2$</td>
<td>-0.70</td>
<td>-</td>
<td>-</td>
<td>2.16</td>
<td>41$^k$</td>
<td>$\sim 11,400$ (104)</td>
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<tr>
<td>13</td>
<td>Cu(Ssal)$_2$ en</td>
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<td>49</td>
<td>1.25$^q$</td>
<td>p</td>
<td>12,800 (80)</td>
<td>13,000 (203)</td>
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<tr>
<td>14</td>
<td>Cu(oac)$_2$ en</td>
<td>-1.54</td>
<td>66</td>
<td>1.00</td>
<td>(8)$^{m}$</td>
<td>14,600 (170)</td>
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<tr>
<td>15</td>
<td>Cu(Me-PhlMe)$_2$</td>
<td>-0.96</td>
<td>58</td>
<td>1.09</td>
<td>p</td>
<td>16,200 (81)</td>
<td>16,000 (92)</td>
<td></td>
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<tr>
<td>16</td>
<td>Cu(IP-PhlMe)$_2$</td>
<td>-0.78</td>
<td>57</td>
<td>1.09</td>
<td>p</td>
<td>$\sim 13,900$ (108)</td>
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<tr>
<td>17</td>
<td>Cu(MeHMe)$_2$ en</td>
<td>-1.50</td>
<td>54</td>
<td>1.05</td>
<td>8$^{n}$</td>
<td>18,400 (177)$^x$</td>
<td>18,300 (207)$^x$</td>
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<td>56</td>
<td>-</td>
<td>np</td>
<td>$\sim 14,800$ (219)</td>
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<td>-1.41</td>
<td>55</td>
<td>-</td>
<td>p</td>
<td>15,600 (131)</td>
<td>16,300 (95)</td>
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<td>51</td>
<td>-</td>
<td>p</td>
<td>16,500 (81)</td>
<td>17,600 (132)</td>
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<td>21</td>
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<td>55</td>
<td>-</td>
<td>p</td>
<td>18,000 (81)</td>
<td>17,600 (132)</td>
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<td>Cu(CF$_3$HMe)$_2$ tn</td>
<td>-1.07</td>
<td>58</td>
<td>0.92</td>
<td>p</td>
<td>16,500 (94)</td>
<td>16,300 (76)</td>
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<tr>
<td>23</td>
<td>Cu(S-MeHMe)$_2$ en</td>
<td>-1.07</td>
<td>58</td>
<td>0.92</td>
<td>p</td>
<td>13,800 (36)</td>
<td>13,900 (41)</td>
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<tr>
<td>24</td>
<td>Cu(PhHII)$_2$ en</td>
<td>-1.26</td>
<td>58</td>
<td>-</td>
<td>p</td>
<td>$\sim 14,700$ (321)</td>
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<td>25</td>
<td>Cu(PhHII)$_2$ tn</td>
<td>-1.08</td>
<td>49</td>
<td>-</td>
<td>p</td>
<td>16,200 (118)</td>
<td>16,300 (163)</td>
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<tr>
<td>26</td>
<td>Cu(PhHII)$_2$ bp</td>
<td>-0.82</td>
<td>49</td>
<td>-</td>
<td>np</td>
<td>$\sim 14,300$ (107)</td>
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<tr>
<td>27</td>
<td>Cu(S-PhHII)$_2$ en</td>
<td>-0.87</td>
<td>58</td>
<td>-</td>
<td>p</td>
<td>$\sim 14,000$ (48)</td>
<td></td>
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<tr>
<td>28</td>
<td>Cu(Me$_2$-MeHMe)$_2$</td>
<td>-1.52</td>
<td>53</td>
<td>-</td>
<td>np</td>
<td>7,500 (66)</td>
<td>7,500 (63)</td>
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<tr>
<td>29</td>
<td>Cu(Ph$_2$-MeHMe)$_2$</td>
<td>-0.88</td>
<td>69</td>
<td>1.02</td>
<td>np</td>
<td>5,900 (41)$^a$</td>
<td>6,100 (41)</td>
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<tr>
<td>30</td>
<td>Cu(MeHMe)$_2$ (en)$_2$</td>
<td>-2.26</td>
<td>65</td>
<td>-</td>
<td>p</td>
<td>16,200 (118)</td>
<td>16,300 (163)</td>
<td></td>
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<tr>
<td>31</td>
<td>Cu(Ni-pa)$_2$</td>
<td>-0.69</td>
<td>57</td>
<td>-</td>
<td>$0^p$</td>
<td>$\sim 19,200$ (119)</td>
<td>$\sim 19,200$ (103)</td>
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<td></td>
<td><strong>Cu(Mc-pa)_2</strong></td>
<td><strong>Cu(Bu-pa)_2</strong></td>
<td><strong>Cu(pa)_en</strong></td>
<td><strong>Cu(Me_2-dipyr)_2</strong></td>
<td><strong>[Cu(2,9-Me_2 phen)_2] [ClO_4]_2</strong></td>
<td><strong>[Cu(2,9-Me_2 phen)_2] [ClO_4]_2</strong></td>
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<tr>
<td>32</td>
<td>-0.61</td>
<td>67</td>
<td>-</td>
<td>p</td>
<td>~16,700 (130)</td>
<td>~16,900 (129)</td>
<td></td>
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<tr>
<td>33</td>
<td>-0.46</td>
<td>72</td>
<td>1.02</td>
<td>60°</td>
<td>15,800 (279)</td>
<td>15,400 (234)</td>
<td></td>
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</tr>
<tr>
<td>34</td>
<td>-0.74</td>
<td>57</td>
<td>0.93</td>
<td>p</td>
<td>18,600 (305)</td>
<td>18,100 (256)</td>
<td></td>
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<tr>
<td>35</td>
<td>-0.70</td>
<td>65</td>
<td>0.98</td>
<td>(68)°</td>
<td>10,900 (278)</td>
<td>11,000 (268)</td>
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<tr>
<td>36</td>
<td>+0.64</td>
<td>61</td>
<td>1</td>
<td>np</td>
<td>-</td>
<td>-</td>
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</tr>
<tr>
<td>37</td>
<td>+0.64</td>
<td>60</td>
<td>1</td>
<td>np</td>
<td>-</td>
<td>-</td>
<td></td>
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</table>

*DMF solution.*
*Apparent values, uncorrected for underlying absorption.*
*Cu(oab)_2Br: D. Hall, T. N. Waters, and P. E. Wright, *J. C. S. Dalton,* 1508 (1973).*
*High value attributed to reducible impurity at ca. -1.1 V.*
*One-electron reductions observed by ac polarography.*
*Separate reduction steps not clearly resolved by ac polarography.*
*Weak shoulder at ~8,700 cm⁻¹ (627).*
*Low energy band not detected.*
*Shoulder at ~16,400 (610).*
*Shoulder at ~16,700 (625).*
*Shoulder at ~16,000 (633) (CHCl_3), 16,400 (690) (DMF).*
*Shoulder at 14,500 (693).*
*CCl_4 solution.*
**Cu(5-tBu-sal)₂ bmp(9)**

The Schiff base was prepared in the same manner as for related compounds [37] and the complex was obtained by the method reported for 8 [25]. It was recrystallized from chloroform-heptane and dried in vacuo at 140°C for 2 days; mp 283-285°C. *Anal. calc* for C₃₆H₃₈N₂O₂Cu: C, 72.76; H, 6.45; N, 4.71. *Found*: C, 72.00; H, 6.43; N, 4.45.

**Cu(5-tBu-sal)₂ bn (10)**

The complex was prepared from stoichiometric quantities of the Schiff base [37] in chloroform and Cu(OAc)₂ in hot ethanol and was isolated after partial removal of solvent and addition of n-heptane. The product was recrystallized from chloroform-ethanol; mp ~277°C (dec). *Anal. calc* for C₄₂H₃₈N₂O₂Cu: C, 75.71; H, 5.75; N, 4.20. *Found*: C, 75.73; H, 5.96; N, 4.18.

**Cu₂(sal)₄(bp) (11)**

2,2',6,6'-Tetranitrobiphenyl was prepared as described [38] and converted to the tetraamine [38] by the procedure used for 2,2'-diaminobiphenyl [39]. The ligand was obtained by adding the tetraaminobiphenyl (0.86 g, 0.004 mol) in hot ethanol to salicylaldehyde (1.95 g, 0.016 mol) in ethanol and refluxing the resulting solution until a yellow crystalline precipitate appeared. The mixture was cooled to room temperature and the product was collected. The ligand was recrystallized from chloroform-ethanol and dried at 140°C in vacuo for one day; mp 231-234°C. *Anal. calc* for C₄₀H₃₀N₄O₄: C, 76.18; H, 4.79; N, 8.88. *Found*: C, 76.67; H, 4.58; N, 8.96. The complex was prepared by the same technique which was used for 7 [25], recrystallized from chloroform-ethanol, and dried at 140°C in vacuo for two days; mp > 360°C. *Anal. calc* for C₄₀H₂₆N₄O₄Cu₂: C, 63.74; H, 3.48; N, 7.43; Cu, 16.86. *Found*: C, 63.75; H, 3.42; N, 7.52; Cu, 16.81.

**Cu₂(5-tBu-sal)₄(m-phen)₂ (12)**

The ligand was formed *in situ* by combining 5-t-butyl-salicylaldehyde (1.78 g, 0.01 mol) and m-phenylenediamine (0.54 g, 0.005 mol) in chloroform and then adding an equal volume of ethanol. After the mixture was refluxed for several min, a hot ethanolic solution of Cu(OAc)₂ (0.005 mol) was added. The red-brown complex formed immediately and crystallized after partial removal of solvent and cooling to room temperature. Recrystallization from chloroform-ethanol afforded the product as the chloroform monosolvate. *Anal. calc*
for C₂₇H₆₁Cl₃N₄O₄Cu₂: C, 62.26; H, 5.59; N, 5.10. Found: C, 62.19; H, 6.05; N, 5.01.

**Cu(Ssal)₂ en (13)**

This compound was prepared by the method briefly reported for Cu(p-MeOC₆H₄-Ssal)₂ [40]. Operations up to and including complex formation were conducted under a nitrogen atmosphere. A solution of o-thiocy-anatobenzaldehyde (1.63 g, 0.01 mol) and sodium sulfide nonahydrate (2.50 g, 0.01 mol) in 25 ml of n-butanol was warmed to ~50° for 10 min. Anhydrous sodium sulfate was added to remove the water and the solution was filtered. Ethylenediamine (0.3 g, 0.005 mol) in 10 ml ethanol was added to the filtrate, and the resulting mixture was warmed for 5 min. Complex formation occurred when copper acetate (1.0 g, 0.005 mol) was introduced to the resulting Schiff base. After a short time the complex and copper sulfide precipitated from solution, the precipitate was collected and the complex was separated by extraction with acetone followed by filtration. As the acetone was removed from the filtrate, the complex appeared as purple crystals; mp 231-233°. Anal. calc for C₁₆H₁₄N₂S₂Cu: C, 53.09; H, 3.90; N, 7.74. Found: C, 52.96; H, 3.87; N, 7.63.

**Cu(PhHH)₂ bp (26)**

The sodium salt of 1-phenyl-propane-1,3-dione (6.8 g, 0.04 mol) and 2,2’-diaminobiphenyl (3.7 g, 0.02 mol) were dissolved in 150 ml of methanol and ca. 2 g of 6N H₂SO₄ in a small volume of methanol was added. The reaction mixture was stirred for 2 h, filtered, and the collected solid extracted with chloroform. The extract was combined with the filtrate, the solvent removed, and the residue extracted with hot benzene. The Schiff base crystallized upon cooling the benzene solution and was recrystallized from carbon tetrachloride; mp 211-213°. The complex was prepared by the reaction of stoichiometric amounts of the base in chloroform and Cu(OAc)₂ in ethanol. It was recrystallized from acetonitrile and dried in vacuo at 80° for 24 h; mp 233-235°. Anal. calc for C₃₀H₂₂N₂O₂Cu: C, 71.20; H, 4.38; N, 5.54. Found: C, 70.68; H, 4.38; N, 5.10.

**Cu(S-PhHH)₂ en (27)**

The ligand [41] (0.7 g, 0.002 mol) was partially dissolved in 50 ml of hot chloroform, to which was added a solution of Cu(OAc)₂H₂O (0.4 g, 0.002 mol) in ethanol. The complex precipitated as golden-brown crystals, which were recrystallized from DMF-ethanol and dried in vacuo at 80° for 24 h; mp

Physical measurements

A Princeton Model 170 Electrochemistry System was employed for polarographic, cyclic voltammetric, and controlled potential coulometric experiments. Polarographic measurements were performed at 25.0 ± 0.1°; a dropping mercury electrode was employed except for complexes 36 and 37, which were measured at a rotating platinum electrode. Solutions were ~1 mM in complex and 0.1 M in tetra-n-propylammonium perchlorate as supporting electrolyte. Slopes and half-wave potentials were evaluated from plots of log[i/(i_d-i)] vs E; E₁/2 values are referenced to a saturated calomel electrode. Coulometric determinations were checked against the stable reversible one-electron couple Ru(acac)₃⁻[42] in DMF solution. DMF was purified by distillation from sodium anthracenide, a procedure which increases its cathodic range compared to the usual distillation from anhydrous CuSO₄. Electronic spectra were recorded on a Cary Model 14 spectrophotometer.

RESULTS AND DISCUSSION

Types and structures of complexes

The complexes selected for redox examination are neutral four-coordinate chelate species which contain Cu(II) in their isolated forms. The only exceptions are the cationic species 36 and 37 [36], with the latter being a stable Cu(I) complex. The complexes may be organized into categories defined by their ligand structures (Fig 1 and Table 1): bis-chelate and tetradentate salicylaldiminates (1-22) [including several binuclear species (11, 12)], β-ketoaminates (15-22, 24-26), β-iminoaminates (28-30), and pyrrole-2-aldiminates (31-34); tetradentate thiosalicylaldiminates (13), o-aminobenzaldiminate (14), and β-thioaminates (23, 27); bis(dipyrromethenide) (35); and bis(2,9-dimethyl-o-phenanthrolines) (36, 37). N₂O₂ donor atom sets occur in all complexes except 13, 23, and 27 (N₂S₂) and 14, 28-37 (N₄). Nearly all complexes in each category whose structures are known from X-ray diffraction results have been included in the investigation. The structural feature of principal importance is the departure from planar stereochemistry inherently preferred by Cu(II). A measure of this feature is the dihedral angle between coordination planes or chelate rings [21]. Reported values of either angle are set out in Table 1. Differences between these angles are generally small and are of no

In cases where no direct structural information is available, the probable structures of the Cu(II) complexes are entered in Table 1 as "p" (planar or nearly so) and "np" (nonplanar). These designations follow from known structures of related complexes, ligand stereochemical constraints, or electronic spectral and magnetic information.
Much of this information on which the structural designations in Table 1 are based has been reviewed elsewhere [21,43] and will not be included here. However, several points are noted. From the available evidence it is not clear to what extent the dihedral angles of the bis-chelates 2-4 are retained in solution [21]. However, ligand field spectra have been interpreted to indicate that 3 and 4 [23], as well as 28, 29 [31], and 33 [34], are nonplanar in solutions of noncoordinating solvents. Likewise, spectral data strongly suggest that 16 is nonplanar whereas 15, with the smaller N-substituent, is planar in such solvents [27]. The steric features of the hindered bridging groups 2,2'-biphenylyl (bp), 6,6'-dimethyl-2,2'-biphenylyl (bmp), and 2,2'-binaphthylyl (bn), when incorporated in tetradentate complexes with planar 6-membered chelate rings, are such as to impose a degree of nonplanar coordination [21,25,37], especially in solution [37]. Pseudotetrahedral structures have been found for Cu(sal)2bp (Table 1) and Co(sal)2bmp [44] (dihedral angle 68°). Ligand field spectral similarities amongst 7-12 and 26 support a nonplanar structure for each in solution. Remaining tetradentate Cu(II) complexes with dimethylene (en) or trimethylene (tn) bridges, which lack steric features promoting nonplanar coordination, are known or expected to be essentially planar.

Electrochemical behavior

Conventional dc polarography was applied to some 35 neutral chelate complexes in DMF solution. Electronic spectral comparisons in chloroform and DMF solutions gave no indication of significant structural changes in the noncoordinating and potentially weakly coordinating solvents although some intensity differences, generally small, were found. Spectral data for the lowest energy resolved ligand field bands in the two solvents are included in Table 1 together with slopes and half-wave potentials determined from least squares plots of log[i/i(i-d)] vs E. Precision of E_1/2 values is at least 0.010 V (determined at a d.m.e.). Measurements were confined to cathodic processes. Slopes obtained from current-voltage curves recorded under the diffusion-controlled conditions prevalent in the dc polarographic measurements are tolerably close to the theoretical value of 59 mV for a one-electron process at 25°. Controlled potential coulometric determinations were performed on representative complexes; potentials applied to a Pt working electrode were ca 0.2 V cathodic of E_1/2 values. The n-values listed in Table 1 demonstrate one- and two-electron reductions for mono- and binuclear species, respectively.

An exception is bis(2-hydroxyacetophenone)trimethyleneimino-Cu(II), whose dihedral angle between coordination planes is 34° [45]. In this case, it would appear that steric interactions between methyl and bridge methylene groups are important in stabilizing nonplanar stereochemistry. Similar interactions may obtain in 18, 20, and 22, but are absent in 25. For this reason the lower energy spectral shifts between pairs of en-tn complexes (Table 1) are not considered to signal a major change in stereochemistry. However, some extent of distortion from planarity for tn-bridged complexes in their Cu(II) form cannot be excluded. This nonplanar complex did not yield well-defined electrochemical behavior.
Exceptions are 1 and 4, which appeared to be reduced to Cu(0) under conditions of the coulometric experiment. This behavior may result from the use of a Pt electrode and/or the electrolysis time (ca. 30-45 min) required for complete reduction. For these complexes and for others not subjected to coulometry, polarographic one-electron reductions at the d.m.e. were established by comparison of diffusion currents. The cyclic voltammetry of selected complexes was also examined. In a number of cases (e.g., 6, 7, 23, 33, 35) the observed behavior was consistent with reversible charge transfer \[46\] at sweep rates \(v\) of 10-1,000 mV/sec, as illustrated by the following data (\(\Delta E_p\), mV; \(i_p^{c}/i_p^{a}\); \(i_p^{c}/v^{1/2}\), \(\mu A \ V^{-1/2} \ \text{sec}^{-1/2}\)): 6, 61(4), 1.01(0.02), 13.5(0.2); 7, 63(7), 0.99(0.02), 16.8(0.9); 35, 63(7), 0.95(0.01), 10.4(0.3). Standard deviations are given in parentheses. Voltammograms of 7 and 23 are shown in Fig. 2. In other instances current-voltage characteristics indicated charge-transfer processes which were either quasi-reversible or were succeeded by irreversible chemical reactions \[46\]. In view of these results and the decidedly negative potentials of all neutral complexes, no attempts were made to isolate the reduced forms. Reversibility of the couple \([\text{Cu}(2,9-\text{Me}_2\text{phen})_2]^{2+/+}\) (36,37) was demonstrated by voltammetry of both forms. The electrochemical results are considered adequate to demonstrate that the various Cu(II) complexes undergo one-electron reductions which, at least under diffusion controlled conditions, are reversible or sufficiently close thereto to allow a valid internal comparison of half-wave potentials.

The great majority of the data set out in Table 1 is new. Previously reported potentials for 17 and derivatives \[47\], 23 \[48\], and 36, 37 \[49\] in nonaqueous media are in adequate agreement with those determined in this work and were shown to correspond to Cu(II)/Cu(I) redox. These results are consistent with others, accumulated in studies too numerous to document in full here, which demonstrate that Cu(II) coordinated in diverse bis-chelate, tetradentate, and macrocyclic complexes can be reduced to Cu(I) in processes that are often chemically and electrochemically reversible.

Structural effects on half-wave potentials

With reference to Table 1 and assuming that Cu(I) is four-coordinate and, ligand structure permitting, will tend to assume a degree of tetrahedrality equal to or exceeding that of Cu(II), the following stereochemical changes occur in the redox processes:

\[
\begin{align*}
\text{p-Cu(II)} + e^- & \leftrightarrow \text{p-Cu(I)} & (1) \\
\text{p-Cu(II)} + e^- & \leftrightarrow \text{np-Cu(I)} & (2) \\
\text{np-Cu(II)} + e^- & \leftrightarrow \text{np-Cu(I)} & (3)
\end{align*}
\]

If it applies in any case Reaction (1) occurs in the reduction of 30, whose macrocyclic structure should prevent significantly nonplanar Cu(I) coordination. Reaction (2) is considered likely for other complexes which are planar in their
FIG. 2. Cyclic voltammograms of complexes 7 and 23 in DMF solution recorded at $v = 100$ mV/sec.

Cu(II) forms, including tetradeionate complexes (e.g., 5, 17). The structures of Co(sal)$_2$en(acac) [50] and Co$_2$[(3MeO-sal)$_2$en]$_3$ [51] indicate that tetradeionate ligands can be deformed from coordination planarity in response to the stereochemical tendency of the metal. This reaction should also apply to bis-chelate complexes which are planar in their oxidized forms, inasmuch as there are no constraining effects toward planarity in the Cu(I) forms. Reaction (3) obviously applies to complexes sterically constrained from planarity in their oxidized forms. Inspection of the data in Table 1 reveals some gross effects of structure. The most negative potential ($-2.26$ V) is observed for 30, Reaction (1). With the exception of 28 potentials corresponding to Reaction (3) occur in
the interval of $-0.46$ to $-0.88$ V for neutral Cu(II) species. The majority of potentials assigned to Reaction (2) fall in the range of ca. $-0.6$ to $-1.5$ V, partially overlapping the range for Reaction (3), but much less cathodic than for the assumed single example of Reaction (1).

The preceding observations are derived from data on complexes with different ligand structures. Hence, the potentials are presumably influenced by both ligand structural and electronic properties. To provide a more meaningful assessment of the sensitivity of Cu(II)/Cu(I) potentials to systematic ligand changes which appear principally to alter the stereochemistry of the oxidized and/or reduced members of the various couples, the complexes have been organized into six series A-F specified in Table 2. In order to allow reasonable comparisons of potentials, the complexes in each series belong to a common ligand category and a reference Cu(II) compound, known or assumed to be essentially planar, is defined for each. These compounds have been utilized as planar standards in previous deductions of solution stereochemistry of related complexes from ligand field spectra [21]. Nonplanar structures have been associated with red shifts of ligand field bands relative to these standards (Table 1). It is apparent that in each series the potentials assigned to Reactions (2) and (3) become less cathodic in the order (3) < (2). If the potentials are accorded thermodynamic significance in that $E_{1/2} = E_0$ under the same physical conditions [52] and $\Delta G^0 = -nF\Delta E_0$ (Nernstian reversibility), then in an approximate sense the reference compounds could be considered to represent the free energy content of the real or hypothetical (sterically unstrained) planar Cu(II) members of each couple in a given series. Ascending positive values of $\Delta E_{1/2}$ in Table 2 reflect the increased relative stabilization of Cu(I) afforded by ligand structural features such as large N-substituents (series A, C, E, and F) and bp, bmp, and bn bridging units (series B and D), all of which promote the stability of a nonplanar structure. Another interesting example of this effect is found in comparisons of potentials for complexes which contain en or tn bridges, but are otherwise identical. Two such cases are included in series C and D and two others are furnished by 17-18 and 21-22. $\Delta E_{1/2}$ values ($E_{1/2}(tn) - E_{1/2}(en)$) vary from 0.18 V (24-25) to 0.34 V (21-22) and are interpreted in terms of enhanced stability of the nonplanar Cu(I) forms afforded by the longer and more flexible $(CH_2)_n$ bridge. The data given in Table 1 and the comparisons offered in Table 2 provide the first adequately documented evidence that destabilization of planar Cu(II) and/or stabilization of nonplanar Cu(I), effected predominantly by ligand steric constraints, produces substantial anodic shifts in Cu(II)/Cu(I) potentials. The dipyrrmethenide complex 35 is closely related to bis(3,3',5,5'-tetramethyl-4,4'-dicarboxoxydroxydipyrrmethen- ido)Cu(II), which has the largest dihedral angle known for any Cu(II) complex (Table 1). However, other than noting that its potential falls in the range for Reaction (3), the actual potential value is difficult to interpret in the absence of a planar reference.

Two binuclear complexes, 11 and 12, were included in this investigation in order to see whether any structural changes accompanying reduction at one
COPPER(II) CHELATE COMPLEXES

TABLE 2
Comparative Structural and Electronic Effects on Half-Wave Potentials

<table>
<thead>
<tr>
<th>Series</th>
<th>Reference</th>
<th>Series members (ΔE&lt;sub&gt;1/2&lt;/sub&gt;, V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structural effects</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>Cu(sal)&lt;sub&gt;2&lt;/sub&gt;en (5)</td>
<td>1(0.31), 2(0.35), 3(0.47), 4(0.55)</td>
</tr>
<tr>
<td>B</td>
<td>Cu(sal)&lt;sub&gt;2&lt;/sub&gt;-o-phen (6)</td>
<td>9(0.28), 8,10(0.33), 7(0.36), 12(0.41)</td>
</tr>
<tr>
<td>C</td>
<td>Cu(PhHMe)&lt;sub&gt;2&lt;/sub&gt;en (19)</td>
<td>20(0.27), 15(0.45), 16(0.63)</td>
</tr>
<tr>
<td>D</td>
<td>Cu(PhHH)&lt;sub&gt;2&lt;/sub&gt;en (24)</td>
<td>25(0.18), 26(0.44)</td>
</tr>
<tr>
<td>E</td>
<td>Cu(MeHMe)&lt;sub&gt;2&lt;/sub&gt;en (30)</td>
<td>28(0.74), 29(1.38)</td>
</tr>
<tr>
<td>F</td>
<td>Cu(pa)&lt;sub&gt;2&lt;/sub&gt;en (34)</td>
<td>31(0.05), 32(0.13), 33(0.28)</td>
</tr>
<tr>
<td>Electronic effects - ring substituents</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>Cu(MeHMe)&lt;sub&gt;2&lt;/sub&gt;en (17)</td>
<td>19(0.09), 21(0.42)</td>
</tr>
<tr>
<td>H</td>
<td>Cu(MeHMe)&lt;sub&gt;2&lt;/sub&gt;tn (18)</td>
<td>20(0.08), 22(0.48)</td>
</tr>
<tr>
<td></td>
<td>Donor atoms&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>Cu(sal)&lt;sub&gt;2&lt;/sub&gt;en (5)*</td>
<td>14&lt;sup&gt;†&lt;/sup&gt;(-0.33), 13&lt;sup&gt;‡&lt;/sup&gt;(0.38)</td>
</tr>
<tr>
<td>J</td>
<td>Cu(MeHMe)&lt;sub&gt;2&lt;/sub&gt;en (17)*</td>
<td>30&lt;sup&gt;†&lt;/sup&gt;(-0.76), 23&lt;sup&gt;‡&lt;/sup&gt;(0.43)</td>
</tr>
<tr>
<td>K</td>
<td>Cu(PhHH)&lt;sub&gt;2&lt;/sub&gt;en (24)*</td>
<td>27&lt;sup&gt;‡&lt;/sup&gt;(0.39)</td>
</tr>
</tbody>
</table>

<sup>a</sup>ΔE<sub>1/2</sub> = E<sub>1/2</sub> (complex) - E<sub>1/2</sub> (ref).
<sup>b</sup>Donor atom sets: *N<sub>2</sub>O<sub>2</sub>, †N<sub>4</sub>, ‡N<sub>2</sub>S<sub>2</sub>.

The metal site would affect the redox potential of the other site. Both sites are nonplanar and the structure of Cu<sub>2</sub>(sal)<sub>4</sub>(m-phen)<sub>2</sub> has been determined (Table 1). (t-Bu groups were included in 12 in order to render the complex adequately soluble.) Dc polarography of the two complexes and ac polarography of 12 showed a single two-electron reduction step. However, the latter method when applied to 11 resolved the peak potentials for two one-electron processes separated by 0.12 V, as shown in Fig. 3. In both cases, the effects of reduction at one site are not transmitted very effectively to the other. The Cu...Cu distance in 11, estimated to be ca. 6 Å from molecular models, is somewhat shorter than the 7.4 Å separation calculated from structural data for Cu<sub>2</sub>(sal)<sub>2</sub>(m-phen)<sub>2</sub>. The longer distance, together with the two separate m-phen bridges compared to a common bridge unit in 11, appears to attenuate markedly structural changes in 12 such that both centers effectively have the same potential.

The ability of the tn bridge to sustain a distorted tetrahedral coordination is supported by the spectra and high-spin nature of Co(sal)<sub>2</sub>tn [53]. Co(sal)<sub>2</sub>en is low-spin and planar.
Electronic effects on half-wave potentials

(a) Ring Substituents

Although the effect of substituent variation on half-wave potentials for complexes of apparently constant Cu(II) stereochemistry was not extensively studied, several features are evident in the data of Table 1. Two recent studies [42, 54], among others, have shown that potentials of metal-centered redox processes are affected by chelate ring substituents in a manner which affords linear correlations of $E_{1/2}$ with the appropriate substituent constants. Examples of similar behavior are indicated in series G and H of Table 2. Here the potentials shift to more negative values in the order CF$_3$ < Ph < Me, consistent with increasing electron-releasing tendencies of the groups as expressed by Hammett $\sigma_p$, $\sigma_m$ or inductive constants exclusive of resonance [55]. In the groups 1-4, 15-16, and 31-33 (series A, C, and F), where N-substituent changes alter stereochemistry, decreasingly negative potentials in the orders Me < Et < i-Pr < t-Bu, Me < i-Pr, and H < Me < t-Bu, respectively, run counter to electron-releasing properties. Hence, the order of potentials is dominated by structural changes. On the other hand, the potential increase Ph > Me for 28-29 (series E) may in part derive from electronic effects.
(b) Donor Atoms

The influence of donor atom changes in planar Cu(II) complexes is expressed in series I, J, and K of Table 2, where species with N₂O₂ donor sets are taken as references. The order of increasingly anodic potential shift is N₄ < N₂O₂ < N₂S₂, where only the donor atom portion of the ligand has been varied. The most interesting feature is the substantial and nearly constant anodic shift of \( \sim 0.4 \) V upon replacing oxygen by sulfur. Attempts to prepare stable Cu(II) complexes containing both an N₂S₂ donor set and nonplanar stereochemistry were unsuccessful. However, the available data do show that, relative to the same or similar reference compounds, sulfur donors promote anodic shifts to an extent comparable with those afforded by nonplanar structures.

Lastly, attention is directed to Fig. 4, which compares potentials for synthetic complexes obtained in this and other studies with those of the "blue" copper sites in proteins. To facilitate comparisons potentials not reported vs the standard hydrogen electrode have been referenced to it, requiring addition of +0.25 V to potentials obtained relative to the s.c.e. The data included have been obtained by direct potentiometry or voltammetry, often in different solvents and, in aqueous solution, at near-neutral pH, and no allowance has been made for junction potential effects. Hence, the comparisons are imprecise, but nonetheless illustrative. Included are potentials for the most cathodic and anodic members of the series which reveal structural and donor atom effects. These effects are summarized as follows: (i) nonplanar bis-chelate or tetradentate complexes are easier to reduce than their planar analogs; (ii) rigid planar tetradentate complexes (en-bridged) are more difficult to reduce than less rigid tetradentate (tn-bridged) or electronically similar planar bis-chelate complexes; (iii) complexes which differ only in donor atom sets are more readily reduced in the order N₄ < N₂O₂ < N₂S₂. On the basis of limited cyclic voltammetric data, it is tentatively concluded that (iv) current-voltage characteristics for nonplanar (especially tetradentate) complexes tend to approach more closely those for reversible charge transfer than is usually the case for planar complexes of the same series.

With regard to the values of the potentials relative to a common reference, it is observed, as pointed out above, that the values for the neutral complexes examined here fall well below the protein range. Indeed, a survey of potentials reported for diverse types of Cu(II) complexes reveal that the great majority occur on the negative side of 0 V vs s.h.e. Some of the more positive potentials are included in Fig. 4. While no entirely adequate generalization concerning the relation between ligand type and potential values is apparent from the data, we note that with the exception of the ammine system, the most positive potentials are afforded by unsaturated nitrogen-donor ligands such as imidazole, phenanthrolines, and bipyridyls [17,19,20,64]. This point has been raised earlier [17] and in the interim much evidence has been collected bearing on the ability of such ligands to stabilize low oxidation states, including Cu(I) [65,66]. The potential for 33 is the least negative of all neutral species examined here, and the...
FIG. 4. Schematic representation of Cu(II)/Cu(I) potentials (vs s.h.e.) of “blue” Cu proteins (ref. 1) and synthetic complexes. Ligands: (a) dodecatungstate, [56]; (b) α-diketonebis(thiosemicarbazones), [57]; (c) hemiporphyrizine, [58]; (d) dithiotropolone, [59]; (e) N$_2$ macrocycles, [60-62]; (f) TAAB, (g) TAAB (OMe)$_2$, [63]; (h) py, (i) NH$_3$, (j) imidazole, benzimidazole, (k) en., [20]; (l) 2,9-Me$_2$phen (potentiometric), [64]; (m) 2-Clphen, [64]; (n) 2,2'-biquinolyl, [19].

potentials for the bis(2,9-Me$_2$phen) (36-37) and bis(2,2'-biquinolyl) cases appear to be the most positive known for synthetic complexes. In these instances the ligand structures should destabilize planar Cu(II) and stabilize tetrahedral Cu(I) in a structure possibly quite similar to that of [Cu(py)$_4$]$^+$ [67].
If the study of "blue" copper sites is to be pursued by the model system approach and the attainment of high reduction potentials is considered obligatory to a realistic model, the comparisons of absolute and relative potentials given here might serve as a useful guide. Assuming four-coordinate Cu(I) in the model and the reduced proteins, a potentially suitable ligand structure would include one thiolate sulfur with some or all of the remaining ligands being histidyl groups, and the entire ligand structure constrained toward nonplanar coordination in both redox forms. However, a cautionary note is in order. Based on experience with ferredoxin synthetic analogs [68,69], structural, spectroscopic, and magnetic features of fixed protein oxidation states can be closely approached in models while failing to match redox potentials by as much as ca. 0.5 to 1 V. Not surprisingly, it is much more difficult to reproduce energetics dependent upon free energy changes of the entire protein molecule than to simulate features of a resting oxidation state.

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REFERENCES


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