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Is Ligand Topology an Influence on the Redox Potentials of Copper Complexes?

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Abstract

The known redox potentials of selected Cu^{2+}/Cu^{+} couples complexed with N-, S- and O-donor ligands are empirically correlated with various characteristics of the ligands. Closed (macrocyclic) ligand topology has little significant effect on the $E_{1/2}$ values, but certain branched (tripodal) ligands show a marked influence on the complexes' redox potentials, generally raising $E_{1/2}$ by a few hundred millivolts. Comparison of the empirically computed $E_{1/2}$ for the [Cu(1,4,7-trithiacyclononane)]$^{2+/+}$ couple with an observed value (+0.465 V versus SCE) suggests that the effect of tripod ligands on $E_{1/2}$ is related to the threefold pseudosymmetry of the donor atoms' dispositions.

Introduction

Characterization of the active sites of proteins containing 'blue' copper as having geometrically irregular copper(II) with two sulfur and two nitrogen donors as nearest neighbours [1] has led to concerted efforts to model these centres with synthetic CuN_2S_2 complexes. An increasing amount of attention is being paid to the redox thermodynamics and kinetics of such copper complexes having aromatic nitrogen, thioether, and thiolate ligands, and to seeking correlations between structural and redox characteristics [2, 3].

Structural features which have been put forward as influencing the redox potentials of copper complexes include (i) the types of donor atoms [4], (ii) the geometry of tetracoordinate complexes [5], and (iii) the flexibility of or constraints by the chelating ligands [6]. Thus, the redox potentials of aqueous copper chelates have been correlated [4] with the ligation according to:

$$E_{1/2} = E^{\circ} + \Sigma(n.\Delta E_{\mathrm{L}})$$

where E° is the standard reduction potential of the aqueous Cu^{2+}/Cu^{+} couple (+150 mV), and the summation terms ΔE_{L} are contributions from the n occurrences of a structural feature of type L in the coordination sphere of the copper(II). Donor atom variation ΔE_{L}s correspond to the occurrence of replacement of a solvent molecule by that type of donor atom for up to at least four water replacements.

This approach, which resembles similar empirical treatments for the quantitation of structural influences [7, 8] is being extended to solvents other than water, and beyond the originally discussed donor atom types [2, 9], so that the presence of five-membered chelate rings linked together in the structure has been realized to be a significant structural feature [9].

We wish to draw attention to two other features of data reported in the literature, namely (i) there appears to be a close correlation in many instances between the $E_{1/2}$ values of copper complexes in water and their $E_{1/2}$s in acetonitrile, and (ii) there is a marked structural effect on redox potentials, which is related to the relative disposition symmetry of the donor groups of the chelating ligand.

Results and Discussion

Comparisons [10] of redox potentials reported by different research groups are complicated by the use of different working electrodes, of different reference electrodes, and most significantly, of different solvents. One approach to the last problem has been to estimate the potential shift between two different solvents as a constant quantity, which can be represented by the shift in $E_{1/2}$ of a redox standard such as ferrocene$^{+/0}$ or $[Ru(Acac)_3]^{0/-}$ [11]*. However, this does not compensate precisely for the stabilization of charged redox states by solvent polarity [12], and cannot take into account any effects of specific solvation (i.e. solvent coordination) of copper coordination sites which are not occupied by the chelating ligand.

Thus, we note firstly that examination of $E_{1/2}$ data [13] for pyridyl-thioether chelates in acetonitrile and in water shows that there is a clear relationship between them ($E_{\mathrm{H_2O}}$ [±38] (mV) = $0.90E_{\mathrm{MeCN}} - 4$; coefficient of determination =

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*Acac in the pentane-2,4-dionate anion.

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TABLE 1. Redox potentials of copper(II/I) couples with N-, S- and O-donors

Ligand	Solvent	Donor set	Chelation ring types[a]	E_{adj}[b] (V)	E_{calcd}[c] (V)	$E_{adj} - E_{calc}$ (V)	Reference
pdthx	H_2O	N_2S_2	5,5,5	+0.24	+0.25	−0.01	d
pdthp	H_2O	N_2S_2	5,6,5	+0.32	+0.29	+0.02	d
pdto	H_2O	N_2S_2	6,5,6	+0.44	+0.39	+0.05	d
pdtn	H_2O	N_2S_2	6,6,6	+0.44	+0.39	+0.05	d
pdahx	H_2O	N_4	5,5,5	−0.35	−0.18	−0.17	d
pdahp	H_2O	N_4	5,6,5	−0.26	−0.14	−0.12	d
pdao	H_2O	N_4	6,5,6	−0.06	−0.04	−0.01	d
pdan	H_2O	N_4	6,6,6	+0.12	−0.04	+0.16	d
pma	H_2O	N_2S_2	5,5,5-T	+0.25	+0.27	−0.03	e
dadt	H_2O	N_2S_2	5,6,5	+0.12	+0.04	+0.08	c
mta	H_2O	NS	5	+0.03	+0.07	−0.03	f
$(mta)_2$	H_2O	N_2S_2	5,5	+0.09	+0.13	−0.05	f
ta	H_2O	O_2S	5,5	+0.04	−0.00	+0.04	e
2-dta	H_2O	O_2S_2	5,5,5	+0.15	+0.09	+0.05	e
3-dta	H_2O	O_2S_2	5,6,5	+0.16	+0.14	+0.02	e
pyr	H_2O	N	0	+0.04	+0.05	−0.01	f
$(pyr)_2$	H_2O	N_2	0	+0.12	+0.11	+0.01	f
$(Im)_2$	H_2O	N_2	0	+0.16	+0.11	+0.06	e
Gly_2	H_2O	N_2O_2	5,5	−0.32	−0.20	−0.11	f
pea	H_2O	N_2S	5,6,5-T	+0.44	+0.51	−0.07	e
cis-12-N_2S_2	H_2O	N_2S_2	5,5,5,5-M	−0.04	−0.03	−0.01	g
trans-12-N_2S_2	H_2O	N_2S_2	5,5,5,5-M	+0.02	−0.03	+0.05	g
cis-14-N_2S_2	H_2O	N_2S_2	5,6,5,6-M	−0.08	+0.06	−0.14	g
trans-14-N_2S_2	H_2O	N_2S_2	5,5,6,6-M	+0.11	+0.06	+0.04	g
cis-16-N_2S_2	H_2O	N_2S_2	6,6,6,6-M	+0.27	+0.16	+0.11	g
trans-16-N_2S_2	H_2O	N_2S_2	6,6,6,6-M	+0.24	+0.16	+0.08	g
L5	MeOH	N_2S_2	5,5,5	+0.26	+0.25	+0.01	h
L1.nPr	MeOH	N_2S_2	5,5	+0.33	+0.39	−0.06	h
L4.Ph	MeOH	N_2S_2	5,5	+0.37	+0.39	−0.02	h
L2.tBu	MeOH	N_2S_2	5,5	+0.39	+0.39	+0.00	h
L3.Bzl	MeOH	N_2S_2	5,5	+0.35	+0.39	−0.04	h
12-ane-S_4	H_2O	S_4	5,5,5,5-M	+0.49	+0.40	+0.08	i
13-ane-S_4	H_2O	S_4	5,5,6,5-M	+0.44	+0.45	−0.01	i
14-ane-S_4	H_2O	S_4	5,6,5,6-M	+0.45	+0.50	−0.05	i
15-ane-S_4	H_2O	S_4	5,6,6,6-M	+0.48	+0.59	−0.11	i
16-ane-S_4	H_2O	S_4	6,6,6,6-M	+0.53	+0.59	−0.06	i
Me_2-2,3,2-S_4	H_2O	S_4	5,6,5	+0.66	+0.50	+0.17	i
NTB	MeCN	N_4	5,5,5-T	+0.20	+0.23	−0.04	j
Tpzn	MeCN	N_4	6,6,6-T	+0.50	+0.37	+0.13	k
15-ane-S_5	H_2O	S_5	5,5,5,5,5-M	+0.60	+0.50	+0.10	l
20-ane-S_6	H_2O	S_6	5,5,6,5,5,6-M	+0.56	+0.69	−0.12	l
21-ane-S_6	MeOH	S_6	6,5,6,5,5,6-M	+0.64	+0.73	−0.09	l
14-ane-S_3N	H_2O	S_3N	5,6,5,6-M	+0.24	+0.28	−0.04	l
Et_2-2,3,2-SNNS	H_2O	N_2S_2	5,6,5	+0.08	+0.04	+0.03	l
2,2,2-NSSN	H_2O	N_2S_2	5,5,5	+0.14	−0.01	+0.14	l
2,3,2-NSSN	MeOH	N_2S_2	5,6,5	+0.10	+0.04	+0.06	l
trien	MeOH	N_4	5,5,5	−0.50	−0.44	−0.06	l

[a] M = macrocycle, T = tripod. [b] E_{adj} is related to E°, and is obtained by subtracting 155 mV from aqueous value, 215 mV from MeOH value. Values from MeCN converted to H_2O by $E(H_2O, V) = 0.96E(MeCN) - 0.004$ V. [c] E_{calc} values from criteria given in text and Table 2. [d] Bis(pyridyl)dithioethers; ref. 13. [e] Linear and tripodal amines, thioethers, carboxylic acids; ref. 4. [f] Amines, thioether-carboxylic acids; ref. 14. [g] Amino-thioether macrocycles; ref. 15. [h] Imidazyl-thioethers; ref. 16. [i] Linear and macrocyclic thioethers; ref. 17. [j] Tripodal benzimidazole; ref. 18. [k] Tripodal pyrazole; ref. 19. [l] Linear and macrocyclic amines, thioethers; ref. 20.

0.986). This allows us to estimate water-based $E_{1/2}$s for complexes studied in MeCN, so that the mainly water-based data sample can be expanded (Table 1: the tabulated values are those of $E_{adj} = E_{1/2} - E^\circ$). With the above caveats in mind, we have also added a few data for complexes in methanol solution, making a rough adjustment of potential between this hydroxylic solvent and water by using an estimate of the difference in the $E_{1/2}$ values of the solvated Cu^{2+}/Cu^{+} couples [9].

Secondly, an empirical comparison (Table 1) of unbranched, acyclic ligands' complexes with complexes of macrocyclic and tripodal N,S-ligands through a statistical (multivariate) examination of the data in Table 1 elaborated the results of interest (Table 2). The principal indicated correlates (sulfur-, heterocyclic N- and saturated N-donors, linked five-membered rings, tripodal ligation), all have contributory significance above the 99% level of confidence. In addition, an F-test indicates that the model accounts for the data well beyond that expected for random fitting, with a standard error for the estimates of 91 mV and an overall coefficient of determination of 0.91.

(1) As indicated previously [4], replacement of water by thioether sulfur substantially raises $E_{1/2}$. The effect of nitrogen donors is dependent on whether they are aromatic or saturated, while carboxylate oxygen donors have a relatively weak influence. Close estimation of $E_{1/2}$ for the S_6 macrocycles is noteworthy.

(2) At least within this data set, incorporation of the donors into a macrocyclic structure (i.e. a closed topology) is of little significance. If anything, it raises $E_{1/2}$, which is probably a counterintuitive result, as one might expect most macrocyclic ligands to accede to the tetragonal stereochemistry to which copper(II) coordination is subject (as opposed to copper(I)).

(3) The donor atom disposition factor is revealed by data from chelating agents of the 'tripod' type, the value of $E_{1/2}$ being raised markedly. The tripodal ligands' intrinsic structural feature leading to this $E_{1/2}$-raising effect of could be: (a) their branched topology, or (b) their three-fold (pseudo)symmetry. To distinguish between these two possibilities, we determined the redox potential of the copper complex of a ligand with non-branched topology but a three-fold symmetric disposition of donor atoms, the macrocycle 1,4,7-trithiacyclononane (Ttcn). In 50% aqueous methanol, the Cu(Ttcn)$^{2+/+}$ couple shows Nernstian behaviour at a Pt electrode, with $\Delta E_p{}^\circ$ = 56 ± 2 mV, $D = 1.2 \times 10^{-6}$ cm^2 s^{-1} and $E_{1/2}$ = +0.47 V versus SCE (+0.71 V versus SHE, E_{adj} = +0.56 V). If branched topology was the important feature in determining the redox potentials of these complexes, then for this non-branched ligand's complex we should expect $E_{1/2} = +0.22 \pm 0.10$ V (versus SCE; 250 mV below the observed value). However, addition of the ΔE_L value associated with the tripodal ligands in Tables 1 and 2 brings the computed $E_{1/2}$ to +0.755 V (within 45 mV of the observed value). This indicates that Ttcn shares the $E_{1/2}$-determinative structural property with the tripod ligands, which property thus cannot be branched topology, but instead a constrained pseudo-threefold donor symmetry. This effect persists in redox data for macrocyclic aliphatic amines [21], despite overshadowing by the strong ligand solvation that is well-known for such systems [22].

TABLE 2. Results from analysis of Table 1 data

Variable feature	ΔE (mV)	Error[a] (mV)	Significance level (%)[b]
Thioether donor	+141	±12	>99.99
Aromatic N-donor	+52	±13	>99.9
Aliphatic N-donor	−75	±12	>99.99
Carboxylate donor	−26	±23	70
Macrocyclic ligand	+24	±44	40
5-Rings linked in chelate	−46	±10	>99.99
Tripodal ligand	+291	±52	>99.99

[a] Standard error of the estimate of ΔE. [b] From t-test.

The structural features of the ligand–copper *complexes* which relate to this E°-enhancement are not immediately clear. An obvious feature of the NTB, Peas and Pmas chelates' stereochemistries is that the copper(II) is distorted away from the tetragonal [18, 23]. This makes appealing the idea that 'tetrahedral distortion' of the otherwise tetragonally based set of principal donors to the copper does indeed raise the $E_{1/2}$ for a pentacoordinate copper(II), just as it does for tetracoordinate copper (even though there is no evidence for *kinetic* manifestation of this in the reduction of the copper(II) [3]). However, for trigonal versus tetragonal symmetry *per se* at the often pentacoordinate Cu^{2+} ion, there is no clear relevance [9]; indeed, the $E_{1/2}$ (DMF) of Cu(Tepa)Cl$^+$ ($\tau = 0.19$ [24]*) is half a volt *higher* than that of Cu(Tmpa)Cl$^+$, although the latter has the more trigonal structure ($\tau = 1.00$) [25].

Experimental

Ttcn and hydrated $Cu(ClO_4)_2$ were obtained from Aldrich and Fluka respectively. The cyclic voltammetry was performed on a L:Cu = 0.95:1.00 (2.37 mM Cu^{2+}) solution at 20 °C in 0.1 M KNO_3 solution deoxygenated by bubbling liquid N_2 boil-off (MG Industrial Gases). The three-electrode cell was driven by PAR-173-based electronics [2] and incorporated a Bioanalytical Systems Pt-disc working electrode and a Beckman saturated calomel electrode.

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*τ is an index of trigonality.

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