Notes

Unusually High Redox Potentials of Two Copper(II) Compounds of 1,8-Bis(3,5-dimethyl-1-pyrazolyl)-3,6-dithiaoctane

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Introduction

Our investigations[1,2] of low molecular weight coordination compounds as models[3] for the active sites in metalloproteins have mainly been focused on structural resemblances. The N_2S_2-donor ligand 1,8-bis(3,5-dimethyl-1-pyrazolyl)-3,6-dithiaoctane[4] (abbreviated as bddo), see Figure 1, meant to model the blue-copper site,[5] was designed to form large coordination angles at the coordinated metal atom. In this paper the remarkable electrochemistry of the compounds $Cu(bddo)(H_2O)(BF_4)_2$ and $Cu(bddo)(H_2O)(ClO_4)_2$ is reported.

Experimental Section

The compounds are very soluble in acetonitrile, rendering dark green solutions. However, with dmso or dmf as the solvent, the color is dramatically less intense. Probably, reduction of copper(II) to copper(I) takes place. *Caution*: Perchlorates may explode violently.

The synthesis of the ligand and the method to prepare the coordination compounds as well as the characterization methods have been described elsewhere.[1,4] The electronic spectra (diffuse reflectance of the solid state in the vis–near-IR region) rendered the following absorption bands: 16.1, 13.2, 10.2 × 10^3 cm^{-1} for $Cu(bddo)(H_2O)(BF_4)_2$ and 15.9, 12.7, 10.3 × 10^3 cm^{-1} for $Cu(bddo)(H_2O)(ClO_4)_2$.

Anal. Found (calcd) for $Cu(bddo)(H_2O)(BF_4)_2$: C, 32.6 (32.4); H, 4.9 (4.8); N, 9.5 (9.4). $Cu(bddo)(H_2O)(ClO_4)_2$: C, 31.3 (31.1); H, 4.6 (4.6); N, 8.9 (9.1).

Cyclic voltammograms were obtained with a PAR Model 174 polarographic analyzer, a PAR Model 175 universal programmer, and a Houston Omnigraph 2000 X-Y recorder. A Metrohm electrolysis cell, Model EA 876/5, was used, with a three-electrode system: a platinum bead (ca. 9.1 mm^2 in area) as working electrode, a platinum spiral as counter electrode, and a Metrohm EA 441/1 saturated calomel electrode as reference. Potentials are quoted versus SCE and are uncorrected for liquid junction potentials and *iR* drop. Peak currents were corrected for background currents, whenever relevant. Experiments were carried out at 25.0 ± 0.1 °C. During the experiments the solutions were kept under a blanket of oxygen-free nitrogen and TEAP (tetraethylammonium perchlorate) was used as supporting electrolyte (see ref 7 for more details). Under these experimental conditions the Fc^+/Fc (Fc = ferrocene) couple gave $E_{1/2} = 345$ mV ($\Delta E = 70$ mV) in the presence of TEAP. These results were used in two ways: criterion for electrochemical reversibility and number of electrons involved; test on the reliability of the behavior of the reference system (SCE and salt bridge), by the occasional check on the reproducibility of the values of the Fc^+/Fc couple.

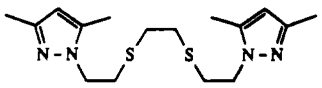

Figure 1. Schematic drawing of the ligand bddo.

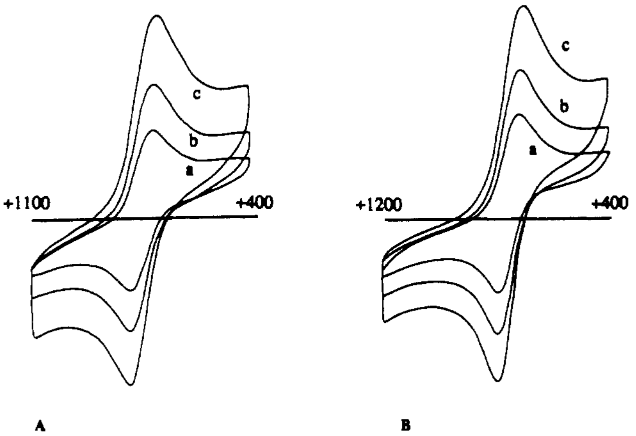

Figure 2. Cyclic voltammograms of $Cu(bddo)(H_2O)(BF_4)_2$ (A) and of $Cu(bddo)(H_2O)(ClO_4)_2$ (B) in acetonitrile at different scan rates: a, 50; b, 100; c, 200 mV/s.

Results and Discussion

The compounds $Cu(bddo)(H_2O)(BF_4)_2$ and $Cu(bddo)(H_2O)(ClO_4)_2$ possess very high redox potentials,[6] as can be noted from the electrochemical data, which are listed in Table I, and from the cyclic voltammograms of these compounds in acetonitrile at different scan rates, which are depicted in Figure 2. Coordination compounds with comparable ligands show redox potentials[7] of ca. 300 to 400 mV (versus SCE), while type I copper proteins show redox potentials of 0.3–0.8 V (versus SHE).[8] The ΔE values of the two complexes (Table I) are comparable to the 70 mV found for the ferricinium/ferrocene couple under the same experimental conditions, indicating that these are electrochemically reversible, one-electron redox processes. The peak current ratios confirm this reversibility.

To investigate which species is responsible for the very high redox potential, the cyclic voltammograms of the hydrated metal salts and of the free ligand in acetonitrile were also recorded: The ligand bddo is not electroactive in the applied potential range. The hydrated metal salts show somewhat higher redox potentials in acetonitrile (see Table I), although the large ΔE values indicate less reversible processes. These results indicate that the ligand bddo is essential for the observed high redox potential of the copper(II) bddo compounds. Within experimental error both compounds have the same half-wave potentials (see Table I), indicating that the noncoordinating anions have a negligible contribution to the observed behavior. The cyclic voltammogram of a copper(II) compound of bddo with a coordinating anion,

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Table I. Electrochemical Data[a] for the Compounds $Cu(bddo)(H_2O)(BF_4)_2$ and $Cu(bddo)(H_2O)(ClO_4)_2$ in Acetonitrile Solution

compound	SR[b]	ΔE	$E_{1/2}$	$i_{p,a}/i_{p,c}$
$Cu(bddo)(H_2O)(BF_4)_2$	50	70	755	1.00
	100	70	755	0.97
	200	70	755	0.97
$Cu(bddo)(H_2O)(ClO_4)_2$	50	70	755	1.0
	100	70	755	0.98
	200	80	750	0.98
$Cu(H_2O)_6(BF_4)_2$	50	90	935	0.95
	100	90	935	0.80
	200	110	945	0.77
$Cu(H_2O)_6(ClO_4)_2$	50	135	938	0.97
	100	160	940	0.89
	200	200	940	0.74
$Cu(bddo)Cl_2$[c]	50	155	513	0.80
	100	155	513	0.81
	200	175	510	0.87

[a] Potentials in V versus SCE, uncertainty ca. 10 mV, all solutions (about 10^{-3} M) were freshly prepared. See also Experimental Section. [b] Scan rate in V/s. [c] See also ref 1.

viz. $Cu(bddo)Cl_2$ in the green modification,[1] shows a normal half-wave potential (see Table I). This suggests that the presence of the noncoordinating anions BF_4 and ClO_4 is required also to obtain the high redox potentials.

When copper(II) tetrafluoroborate or copper(II) perchlorate are dissolved in acetonitrile, a weakly blue colored solution is obtained. Upon addition of an equimolar amount of the ligand bddo, the color of the solution turns immediately to dark green. Electron spectroscopy of these solutions shows a change in the location of the absorption maxima, from ca. 13.2×10^3 to 15.2×10^3 cm^{-1}, and a 15-fold increase in the molar absorptivity.

The cyclic voltammetry shows the presence of a reversible process, which suggests that the reduced species must also be stable in solution, possibly due to the formation of a (pseudo-)tetrahedral tetradentate copper(I) coordination by the ligand bddo.[9] However, a solid copper(I) tetrafluoroborate compound with bddo could not be isolated, despite several attempts using different solvents.

Conclusion

The present study shows that a copper(II) compound coordinated by a relatively flexible ligand may have a high redox potential. This indicates that the often assumed rigid structure exerted by the protein on the shape of the active site is not a prerequisite for the high redox potential.[10]

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