Spectrophotometric Study of the Stabilities of Copper, Zinc, Nickel and Cobalt Complexes with 1,2-Bis-methyl(2-aminocyclopentene carbodithioate)ethane in Binary *N,N*-Dimethyl Formamide Dichloromethane Mixtures

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Interest in coordination compounds with nitrogen and sulfur donor groups stems from the surprising physical properties of metalloenzyme active sites which involve similar coordination and participation in electron transfer reactions.¹⁻⁵ The complex of 1,2-bis-methyl(2-aminocyclopentene carbodithioate)ethane (BMACD) and copper(II) has been found to be a good model which can mimic the properties of blue copper(II) protein.¹ Bereman and co-workers² reported the complexation of Ni(II) and Cu(II) with the above ligand.

Consistent among many of the proposed coordination environments for several quite varied metalloenzymes is a distorted four coordinate N_2S_2 donor set. Since the discovery of the nickel centers in certain hydrogenases, CO dehydrogenases and methyl coenzyme reductases, efforts have also centered around defining the stabilizing effects which nitrogen and sulfur donor atoms exert on nickel in various oxidation states.⁶⁻⁸ Common to many proposed active site models are combinations of sulfur, nitrogen and oxygen donors in planar and distorted four coordinate environments.

The work by Bereman and coworkers produced the series of related tetradentate N_2S_2 ligands *N,N'*-ethylene-bis-, trimethylene-bis-, and tetramethylene-bis(methyl 2-amino-1-cyclopentene dithiocarboxylate), which, when chelated to Cu(II) and Ni(II) trapped stereochemistries at various points along the square planar tetrahedral equilibrium (Fig. 1).^{9,10} Later, Bereman and coworkers² attempted to stabilize even more distorted Ni(II) and Cu(II) complexes by both extending the methylene bridge between nitrogens and adding progressively bulkier aliphatic residues to the parent methyl-2-aminocyclopentene dithiocarboxylate ligands. They proposed the stereochemistries on the basis of ESR parameters and NMR spectral data of the respective Cu(II) and Ni(II) complexes. We have recently found that BMACD can selectively transport copper through a liquid membrane.⁶

Metal complexes of BMACD are interesting in light of the continuing interest in the bioinorganic chemistry of some of the transition metals and are also important in studies of "blue copper" proteins. Along this line,

we attempted to study the stoichiometry and stabilities of BMACD complexes with different metal ions. In this paper a spectrophotometric study of BMACD complexes with copper, zinc, nickel ions is described in binary DMF- CH_2Cl_2 mixtures at 25°C.

The influence of solvent properties on the stoichiometry and stabilities of BMACD complexes are discussed.

Experimental

Reagents

Reagent grade nitrate salts of copper, zinc, nickel and cobalt (all from Merck) were used without further purification other than drying. *N,N*-Dimethylformamide (Fluka) and dichloromethane (Fluka) mixtures were prepared by weight.

The ligand was synthesized and purified according to the procedure reported by Baird.¹

Apparatus

The spectra were recorded on a Philips 8750 ratio recording spectrophotometer and the absorbance measurements were made with a Philips 8675 visible spectrophotometer at 25±1°C.

Fig. 1 Visible spectra of (1) BMACD (1×10^{-4} M), (2) – (8) similar concentration of BMACD with increasing amounts of copper; (2) 1×10^{-5} M copper and (8) 1×10^{-4} M copper.

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Procedure

The exact amounts of BMACD and of each cation were obtained by weighing. All pieces of volumetric glassware were calibrated.

The formation constants of the 1:1 complexes of BMACD with the cations used were determined accurately by a non-linear least-squares curve fitting program, Kinfit.⁷ Equilibrium was assumed to be attained if there was no further change in the spectra after several hours. It was found that Cu^{2+} forms a 1:1 complex with BMACD instantaneously, while the formation of Zn^{2+} , Ni^{2+} and Co^{2+} complexes with BMACD is slower and takes about an hour.

Results and Discussion

Figure 1 shows the spectra of BMACD and its copper complex. As one can see, the absorbance intensity of BMACD is decreased by the addition of copper ions to the ligand solution. This is also true in the cases of the other metal ions tested. The change in absorbance at the wavelength of maximum absorption, λ_{max} , of the ligand (406 nm) was used for the calculation of stability constants of the corresponding metal BMACD complexes. Therefore, the concentration of BMACD was kept constant while the concentrations of metal ions were varied.

The stoichiometry of copper, zinc, nickel and cobalt complexes with BMACD in different DMF- CH_2Cl_2 mixtures were determined by a mole ratio method.^{8,9} It was found that, in the case of all complexes studied, the mole ratio of metal ion to BMACD was 1:1. Figure 2 shows a typical mole ratio plot for copper-BMACD complex in 60% CH_2Cl_2 -DMF mixture.

All calculated formation constants for the resulting complexes between metal ions studied and BMACD in different binary DMF- CH_2Cl_2 mixtures are listed in

Fig. 2 Mole-ratio plot for BMACD- Cu^{2+} complex in 60% CH_2Cl_2 /DMF mixture. "o" denotes the observed data; "x" denotes the corresponding value expected from computer fit and "=" shows the points where the observed and expected values are superimposed on each other.

Table 1 and the relationship between the logarithm of the formation constants of the complexes and the mole fraction of dichloromethane in DMF is shown in Fig. 3. As is clear from this figure, in all solvent mixtures used, the stability observed for BMACD complexes are in the order $\text{Zn}^{2+} < \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+}$; thus the trend follows the Irving-Williams series.

Figure 3 also shows the influence of solvent properties on the stabilities of BMACD complexes. As one may see, in the case of all metals used, there is a linear relationship between the complex stability and the mole fraction of dichloromethane in the solvent mixture. In other words, there is an inverse relationship between the solvating ability of the solvent and the stability of the complexes. It is obvious that DMF with a relatively high solvating ability ($\text{DN}=26.6$), can compete with BMACD for the cations, compared to CH_2Cl_2 which is a solvent of very low solvating ability ($\text{DN}=0$). However, a sharp increase in K_f upon addition of CH_2Cl_2 to DMF was not observed most probably because CH_2Cl_2 is a solvent with a low dielectric constant ($D=9.08$) compared to that of DMF ($D=36$) and thus the contribution of ion pairing upon addition of CH_2Cl_2 is expected to be more pronounced than in DMF solutions.

Therefore, the presence of an increasing amount of CH_2Cl_2 in the solution would cause ion pair formation to be more pronounced and this will consequently compromise to some extent the effect of low solvating ability of CH_2Cl_2 . The net effect will be a slow increase in the $\log K_f$ values upon increasing addition of CH_2Cl_2 to DMF solutions (Fig. 3).

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Fig. 3 Variation of $\log K_f$ vs. $X_{\text{CH}_2\text{Cl}_2}$ for BMACD complexes of Cu^{2+} , Ni^{2+} , Co^{2+} and Zn^{2+} ions.

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