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LETTER

Heterobinuclear (Cu–M) complexes containing an endogenous benzimidazolate bridge

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Abstract

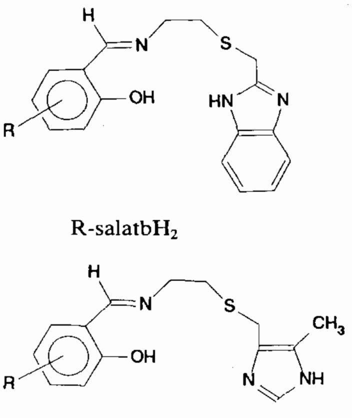
We report two new (Cu–M) heterobinuclear complexes containing an endogenous benzimidazolate bridge. In the reaction of $Cu(hfac)_2$ and the neutral cadmium complex to prepare the heterobinuclear complex, a metal exchange reaction has occurred. Both complexes contain the copper(II) ion in an N_2SO environment.

Introduction

The active sites of copper proteins, for which X-ray crystal structures are available, contain Cu(II) bound by two or more histidine groups [1]. Imidazole-containing Schiff-base ligands can act as versatile models for copper environments [2] and provide the opportunity to study Type 2 copper sites such as that present in bovine erythrocyte superoxide dismutase (BESOD) where an imidazolate bridges the heterobinuclear copper–zinc pair [3].

A general method of forming imidazole or benzimidazole bridges between similar and dissimilar metal uses unsymmetrical tetradentate ligands containing an imidazolate fragment and some binuclear complexes with this type of bridge have been reported [4].

In previous papers [5, 6] we have described some neutral and cationic complexes with ligands such as those depicted in Scheme 1 which involve salicylaldehyde, thioether and imidazole or benzimidazole groups that provide an N_2SO environment around the metal. The neutral complexes [6] contain both deprotonated salicylaldehyde and benzimidazole or imidazole groups and can act as ligands through the second nitrogen atom of the benzimidazolate or imidazolate group. Interaction with compounds such as metal halides, nitrates or hexafluoroacetylacetonates can lead to the preparation of homo- and heterobinuclear complexes.



R-salatbH_2

R-salatmiH_2

Scheme 1.

Experimental

Physical measurements

Microanalyses were determined using a Perkin-Elmer 240B microanalyser. IR spectra were recorded as KBr discs or Nujol mulls using a Perkin-Elmer 180 spectrometer, diffuse reflectance spectra of solids using a Philips Scientific SP 700 spectrometer and fast atom bombardment mass spectra on a Kratos MS50TC spectrometer. The ESR spectrum was recorded on a Bruker ER 200D spectrometer.

Reagents and preparations

All reagents were of the highest grade commercially available and were used as received. The Schiff-base ligands (5-Br-salatbH_2 and 5-OMe-salatbH_2) were prepared by the method described in ref. 5. The ligand 5-OMe-salHatbH_2 was synthesized by reduction of the imine bond with sodium borohydride. [Cu(5-Br-salatb)]·$3H_2O$ and [Cd(5-OMe-salHatb)]·$2.5H_2O$ were prepared by an electrochemical procedure as described in previous papers [6].

[Cu(5-Br-salatb)Zn(hfac)$_2$]·$3H_2O$

[Cu(5-Br-salatb)]·$3H_2O$ (0.0800 g) was suspended in chloroform (50 ml) and gently refluxed for 1 h. Addition of $[Zn(hfac)_2]\cdot 2H_2O$ (0.0814 g) gave a dark solution which was gently refluxed with stirring for *c.* 4 h. Evaporation of the solvent gave a black solid which

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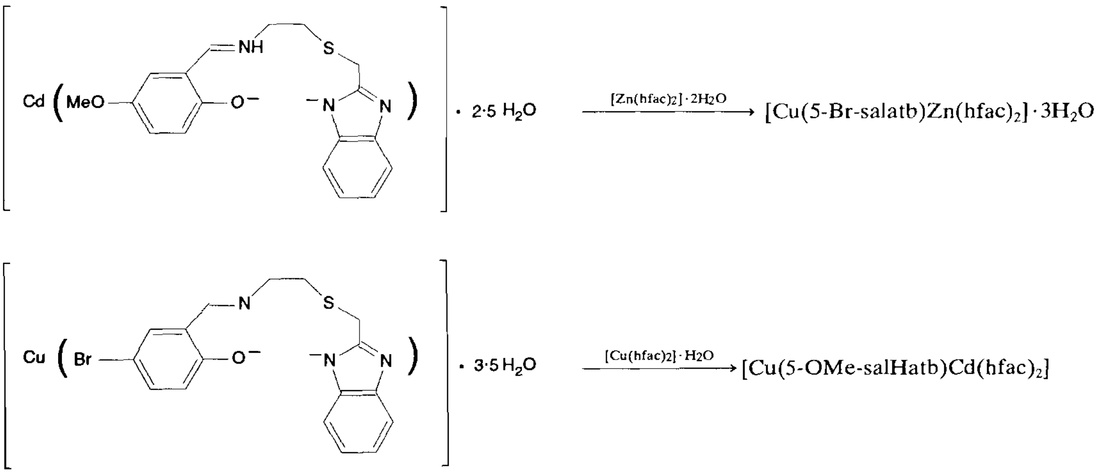

Scheme 2.

was filtered off and dried under vacuum. *Anal.* Found: C, 34.07; H, 2.20; N, 3.95. Calc. for $BrC_{27}CuF_{12}H_{22}N_3O_8SZn$: C, 34.00; H, 2.30; N, 4.41%. IR (Nujol mull): 3500br, 1640vs, 1620sh, 1600sh, 1550m, 1530m, 1250vs,br, 1200vs,br, 1140vs,br, 800s, 670s, 590s, 530m.

[Cu(5-OMe-salHatb)Cd(hfac)$_2$]

[Cd(5-OMe-salHatb)]·$2.5H_2O$ (0.0700 g) was suspended in chloroform (5 ml) and gently refluxed for *c.* 20 min. A solution of [Cu(hfac)$_2$]·H_2O (0.0606 g) in chloroform (5 ml) was added dropwise to the former suspension giving a dark brown solution which was gently refluxed with stirring for *c.* 7 h. Slow evaporation of the solvent gave a black solid which was filtered off and dried under vacuum. *Anal.* Found: C, 36.91; H, 2.39; N, 4.58. Calc. for $C_{28}CdCuF_{12}H_{21}N_3O_6S$: C, 36.09; H, 2.26; N, 4.51%. IR (Nujol mull): 1650s,br, 1610vw, 1555m, 1530m, 1490sh, 1280sh, 1255s, 1200s, 1140s,br, 1085w, 790m, 760sh, 740m,br, 720w, 665m, 580m, 520vw.

Results and discussion

The neutral mononuclear complexes, [Cu(5-Br-salatb)]·$3H_2O$ and [Cd(5-OMe-salHatb)]·$2.5H_2O$, were found to be insoluble in common organic solvents. This property indicates a probable polynuclear structure for both complexes in which bridging via benzimidazolate nitrogens is likely.

In the synthesis of the M′(hfac)$_2$ adduct it is neither necessary nor possible to dissolve the [ML] complex before mixing the components. As the formation of the adducts proceeds, [ML] is taken up into solution until no solid remains. In contrast to the parent complexes, the M′(hfac)$_2$ adducts are soluble in most organic solvents. The preparation of the adducts is given in Scheme 2.

The IR spectra of these heterobinuclear complexes are different from both those of the starting materials and of deliberately constructed physical mixtures of these materials. The spectra of the adducts show absorptions at 1640vs (ν(C=O)), 800s, (δ(C–H)) and 670 cm^{-1}, as well as three superimposed bands between 1300 and 1100 cm^{-1} (ν(C–F)), attributable to the hexafluoroacetylacetonate fragment. Bands assignable to the tetradentate ligand, L, are also present.

The optical spectrum (diffuse reflectance) of the (Cu–Zn) complex shows absorptions at 15 000 and 22 000sh cm^{-1}. These bands are similar to those in [CuL], L = R-salatb, in which the copper(II) is in an unusually distorted square planar environment where the sulfur atom lies out of the plane containing the Cu, N and O atoms [6]. In the heterobinuclear adduct, the copper(II) seems to remain in that distorted square planar environment, while both hexafluoroacetylacetonates and the benzimidazolate fragment of the tetradentate ligand provide a five coordination around the zinc atom. The FAB mass spectrum in nitrobenzylalcohol does not show the peak corresponding to the binuclear fragment, but contains a peak at 454 assignable to [Cu(5-Br-salatb)] + 1.

The optical spectrum of the (Cu–Cd) adduct formed by reaction of the neutral cadmium compound, [Cd(5-OMe-salHatb)]·$2.5H_2O$, and [Cu(hfac)$_2$]·H_2O shows bands at 16 400 and 21 200sh cm^{-1}. This spectrum suggests that a metal exchange reaction has occurred, facilitated by the site requirements of the individual metals. The [Cu(hfac)$_2$(benzimidazolate)] moiety can be compared to another [Cu(hfac)$_2$(amine)] complex, [Cu(hfac)$_2$(pyridine)] [7]. This species has a ligand field absorption maximum at *c.* 13 000 cm^{-1}. Therefore, if both metal ions, cadmium and copper, were not interchanged, the visible absorption band for the heterobinuclear complex would be expected at higher wavelength than is observed. The complex would then be green in colour, not black, a colour which can only possibly result from low-energy charge-transfer bands in the CuN_2SO chromophore. The FAB mass spectrum in nitrobenzylalcohol and ESR spectrum of the (Cu–Cd) complex support this consideration. A peak at 405 (65%), which corresponds to the fragment [Cu(5-OMe-salHatb)] + 1, is present in the FAB mass spectrum and no peak assignable to [Cd(5-OMe-salHatb)] is detected. The powder ESR spectrum is axial with $g_{\parallel} = 2.45$, $g_{\perp} = 2.10$ and $A_{\parallel} \approx 200$ G. On comparision of these data with those reported for square planar complexes of copper(II) [8, 9] it is evident that the Cu(II) ion in our compound is in a similar environment.

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