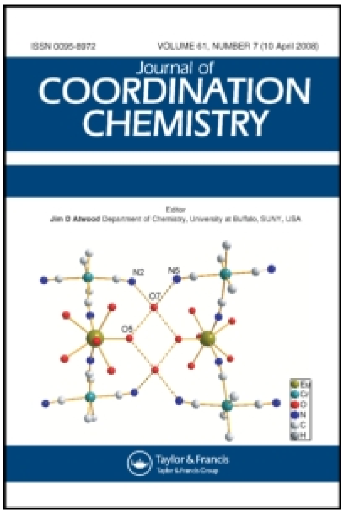

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Liliana Strinna Erre[a]; Beatrice Gulinati[a]; Giovanni Micera[a]; Franco Cariati[b]
[a] Dipartimento di Chimica, Universita di Sassari and lstituto C.N.R. per I'Applicazione delle Tecniche Chimiche Avanzate ai Problemi Agrobiologici, Sassari, Italy [b] Dipartimento di Chimica Inorganica e Metallorganica, Unhersita di Milano, Milan, Italy

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INTERACTION OF METAL IONS WITH HUMIC-LIKE MODELS. PART 11. ADDUCTS OF Cu(II)-2,6-DIMETHOXYBENZOATES WITH HETEROCYCLIC BASES

LILIANA STRINNA ERRE, BEATRICE GULINATI, GIOVANNI MICERA*

Dipartimento di Chimica, Università di Sassari and Istituto C.N.R. per l'Applicazione delle Tecniche Chimiche Avanzate ai Problemi Agrobiologici, Via Vienna 2, 07100 Sassari, Italy

and FRANCO CARIATI

Dipartimento di Chimica Inorganica e Metallorganica, Università di Milano, Via G. Venezian 21, 20133 Milan, Italy

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Adducts formed by the dinuclear complexes $[Cu_2(2,6\text{-DMB})_4(H_2O)_2]$, (I) and $[Cu_2(2,6\text{-DMB})_2(O_2CCH_3)_2(H_2O)_2]$, (II) (2,6-DMB = 2,6-dimethoxybenzoate) with nitrogenous bases [pyridine (py), 4-ethylpyridine (4-Etpy), pyrazine (pz), 2-methylpyrazine (2-Mepz), imidazole (im), 1-methylimidazole (1-Meim) and 2-phenylimidazole (2-Phim)] have been synthesized and characterized. Starting with II, only one adduct, $[Cu_2(2,6\text{-DMB})_2(O_2CCH_3)_2(2\text{-Phim})_2]$, was obtained. In the other cases, starting with either I or II, monomeric compounds containing two 2,6-DMB ligands and one or two base molecules were isolated. The structure of these compounds consists, basically, of tetragonal copper(II) chromophores involving metal coordination by monodentate carboxyl groups and nitrogen atoms in the plane, with water molecules, when present, as axial donors.

Keywords: Copper(II), 2,6-dimethoxybenzoic acid, amine adducts

INTRODUCTION

In the course of a study on metal complexes formed by simple humic-like molecules,[1-10] we have recently reported the structure of the complexes formed by 2,x-dimethoxybenzoic (x = 3, 4, 5 or 6) and 3,y-dimethoxybenzoic (y = 4 or 5) acids with some divalent metal ions.[8-10]

In particular, in the case of the 2,6-DMB ligand, due to the presence of bulky methoxy substituents in positions *ortho* to the carboxyl group, rather unusual structures were observed. In fact, polymeric aqua-bridged complexes were obtained in the case of Mn, Co, Ni and Zn, while two dimeric tetracarboxylate-bridged compounds, $[Cu_2(2,6\text{-DMB})_4(H_2O)_2]$ (I) and $[Cu_2(2,6\text{-DMB})_2(O_2CCH_3)_2(H_2O)_2]$ (II), the former having the typical structure of copper(II) acetate monohydrate and the latter involving two *trans* couples of 2,6-DMB and acetate ligands, were isolated for Cu(II).

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* Author for correspondence.

To ascertain the coordinating properties of this ligand in ternary systems and in particular to determine whether the mixed acetate-2,6-DMB coordination of **II** is preserved in the presence of additional ligands, we have now prepared adducts of the above complexes with heterocyclic amines. Spectroscopic and magnetic properties of the complexes are reported below.

EXPERIMENTAL

Materials

2,6-Dimethoxybenzoic acid, purchased from Fluka, was twice recrystallized from water and dried *in vacuo*. Copper(II) acetate monohydrate and copper(II) nitrate (Carlo Erba) were the metal sources. The bases were used as commercially available products.

Preparation of complexes

$[Cu_2(2,6\text{-}DMB)_4(H_2O)_2]$ (**I**) and $[Cu_2(2,6\text{-}DMB)_2(O_2CCH_3)_2(H_2O)_2]$ (**II**) were prepared as described previously.[8] The synthetic methods for obtaining the adducts were similar for all the complexes. Typically, **I** or **II** (5×10^{-4} mol) was dissolved in methanolic or ethanolic solutions ($50\,cm^3$) containing an excess of amine. On standing at room temperature for several weeks, $[Cu(2,6\text{-}DMB)_2(2\text{-}Mepz)_2]$ lost a base molecule and yielded a 1:1 adduct. A compound exhibiting the same stoichiometry and the same spectral properties was prepared directly by reaction in solution using a copper to amine molar ratio of 1:1. Microcrystalline precipitates were obtained after cooling at 4–5°C. Analytical data are listed in Table I.

TABLE I
Analytical data for the complexes.[a]

Complex	C%	H%	N%	H_2O or MeOH%[b]
$[Cu(2,6\text{-}DMB)_2(py)_2]$	57.65(57.58)	4.96(4.83)	4.61(4.80)	
$[Cu(2,6\text{-}DMB)_2(4\text{-}Etpy)_2]$	60.37(60.04)	6.20(5.67)	4.54(4.38)	
$[Cu(2,6\text{-}DMB)_2(Im)_2(H_2O)_2]\cdot H_2O$	46.95(46.79)	5.09(5.20)	9.29(9.09)	9.0(8.77)
$[Cu(2,6\text{-}DMB)_2(1\text{-}Meim)_2]$	52.63(52.92)	5.58(5.12)	9.40(9.49)	
$[Cu(2,6\text{-}DMB)_2(pz)(H_2O)_2]$	49.24(48.75)	4.40(4.80)	5.66(5.17)	6.5(6.64)
$[Cu(2,6\text{-}DMB)_2(2\text{-}Mepz)_2(H_2O)_2]$	51.83(51.73)	5.14(5.27)	8.64(8.62)	6.0(5.54)
$[Cu(2,6\text{-}DMB)_2(2\text{-}Mepz)]$	51.50(51.25)	4.95(4.91)	5.23(5.09)	
$[Cu(2,6\text{-}DMB)_2(2\text{-}Mepz)_2]$	55.18(54.76)	5.25(4.92)	8.90(9.12)	
$[Cu(2,6\text{-}DMB)_2(2\text{-}Phim)_2]\cdot 1.5\,MeOH$	59.87(59.09)	5.77(5.29)	7.46(7.38)	7.0(6.30)
$[Cu_2(2,6\text{-}DMB)_2(O_2CCH_3)_2(2\text{-}Phim)_2]$	53.28(53.63)	4.67(4.50)	6.12(6.25)	

[a] Calculated values in parentheses. [b] Thermogravimetric determination.

The compounds containing water (or MeOH) were dehydrated by heating. The appropriate temperature ranges were selected on the basis of thermogravimetric analyses.

Instruments

Thermogravimetric data were obtained with a Perkin-Elmer TGS-2 apparatus in nitrogen or air atmosphere. A scanning rate of 5°C min^{-1} was employed. Chemical analyses were performed on a Perkin-Elmer 240 B elemental analyser. IR spectra were recorded on a Perkin-Elmer 683 B spectrophotometer in KBr disks (4000–600 cm^{-1}), powdered samples spread on NaCl plates (1700–1200 cm^{-1}) or as nujol mulls between polyethylene disks (600–200 cm^{-1}). Electronic diffuse reflectance spectra were obtained by use of a Beckman Acta M IV spectrophotometer with $BaSO_4$ as the reference sample. ESR spectra were measured on a Varian E 9 spectrometer at the X-band frequency. Magnetic susceptibility data were measured at room temperature using a Bruker B-MB4 system and corrected for diamagnetism using Pascal's constants.

RESULTS AND DISCUSSION

General Trends

Reaction of the dinuclear complexes $[Cu_2(2,6\text{-DMB})_4(H_2O)_2]$ (**I**) and $[Cu_2(2,6\text{-DMB})_2(O_2CCH_3)_2(H_2O)_2]$ (**II**) with nitrogenous bases afforded mono- and bis-adducts containing, in some cases, water or solvent molecules. In particular, according to the elemental analysis, mono-adducts were obtained only with pyrazine, 2-methylpyrazine and 2-phenylimidazole. Bis-adducts were obtained with all the bases except pyrazine and 2-phenylimidazole. By starting from **II**, only in one case was an adduct containing both 2,6-DMB and acetate ligands obtained, $[Cu_2(2,6\text{-DMB})_2(O_2CCH_3)_2(2\text{-Phim})_2]$. In all other cases, starting from either **I** or **II**, compounds containing two 2,6-DMB ligands per copper ion were isolated. Based on the analytical, spectroscopic and magnetic data, certain conclusions may be drawn concerning the structure of the complexes.

Magnetic, ESR and Electronic Data

The complex $[Cu_2(2,6\text{-DMB})_2(O_2CH_3)_2(2\text{-Phim})_2]$ exhibits magnetic and ESR properties (Table II) similar to those of the tetracarboxylate-bridged dinuclear species **II** and thus the presence of an analogous entity, involving a base molecule in the place of water in the fifth coordination position of the copper ion may be suggested.

On the contrary, the compounds containing two 2,6-DMB ligand molecules per copper ion have properties typical of complexes without strong metal–metal interactions (Figures 1 and 2, Table II). ESR spectra are of the axial type with g-values indicative of tetragonally elongated geometry involving nitrogen atoms in the metal plane. Exceptions are for $[Cu(2,6\text{-DMB})_2(2\text{-Mepz})_2(H_2O)_2]$, which exhibits a clearly resolved three g value spectrum suggesting rhombic distortion, and the bis-adducts $[Cu(2,6\text{-DMB})_2(Im)_2(H_2O)_2]\cdot H_2O$ and $[Cu(2,6\text{-DMB})_2(1\text{-Meim})_2]$, for which spectra unresolved in the parallel region, and thus uninformative, are detected. On the other hand, the rather narrow ESR resonances observed for the mono-adduct $[Cu(2,6\text{-DMB})_2(pz)(H_2O)_2]$ (and its dehydrated product) may be indicative of exchange interactions due to bidentate bridging of the base, as is known with pyrazine.[11–12]

TABLE II
Spectroscopic data for the complexes.

Complex	ESR parameters	Absorption maxima (10^3 cm^{-1})	μ(B.M.)
[Cu(2,6-DMB)$_2$(py)$_2$]	2.253, 2.060	17.2, 15.4sh	1.89
[Cu(2,6-DMB)$_2$(4-Etpy)$_2$]	2.238, 2.053	17.8, 15.4sh	2.26
[Cu(2,6-DMB)$_2$(Im)$_2$(H$_2$O)$_2$]·H$_2$O		15.9, 14.3sh	2.02
[Cu(2,6-DMB)$_2$(Im)$_2$][a]	2.224, 2.072	17.2, 15.4sh	
[Cu(2,6-DMB)$_2$(1-Meim)$_2$]		18.2, 15.3sh	1.89
[Cu(2,6-DMB)$_2$(pz)(H$_2$O)$_2$]	2.310, 2.070	15.1	1.79
[Cu(2,6-DMB)$_2$(pz)][a]	2.259, 2.060	17.2, 15.4sh	
[Cu(2,6-DMB)$_2$(2-Mepz)$_2$(H$_2$O)$_2$]	2.318, 2.089, 2.056	14.4	2.09
[Cu(2,6-DMB)$_2$(2-Mepz)]	2.297, 2.080	15.6, 14.3sh	1.82
[Cu(2,6-DMB)$_2$(2-Mepz)$_2$]	2.228, 2.056	17.2, 15.4sh	1.98
[Cu(2,6-DMB)$_2$(2-Phim)$_2$]·1.5 MeOH	2.327, 2.070	13.7	2.13
[Cu$_2$(2,6-DMB)$_2$(O$_2$CCH$_3$)$_2$(2-Phim)$_2$]	2.38, 2.08[b]	13.6	1.66

[a] Obtained by heating. [b] D = 0.37 cm^{-1}.

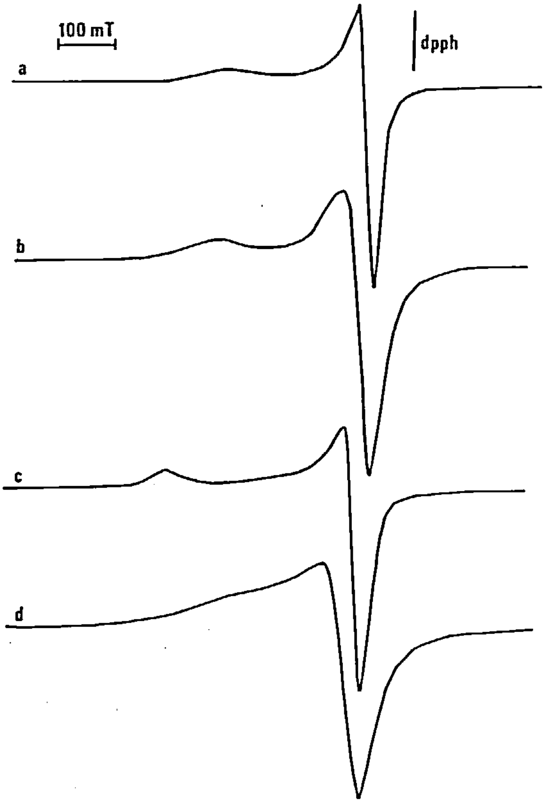

FIGURE 1 X-Band ESR spectra of [Cu(2,6-DMB)$_2$(4-Etpy)$_2$] (a), [Cu(2,6-DMB)$_2$(py)$_2$] (b), [Cu(2,6-DMB)$_2$(2-Phim)$_2$]·1.5 MeOH (c), and [Cu(2,6-DMB)$_2$(Im)$_2$] (d).

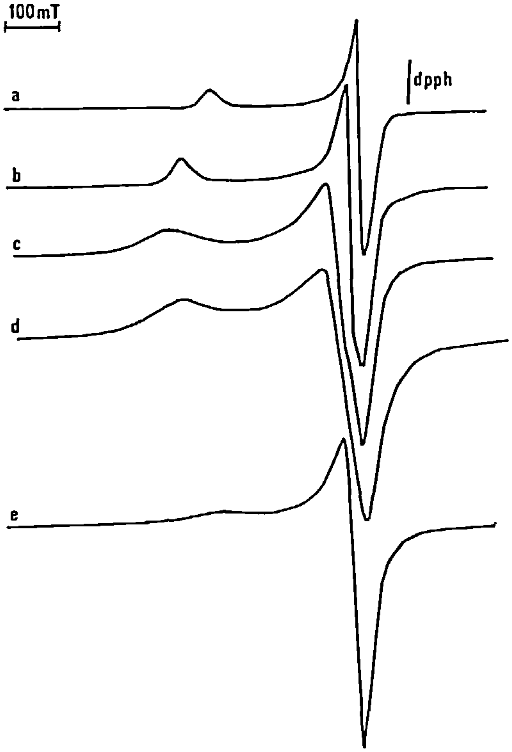

FIGURE 2 X-Band ESR spectra of $[Cu(2,6\text{-}DMB)_2(pz)]$ (a), $[Cu(2,6\text{-}DMB)_2(pz)(H_2O)_2]$ (b), $[Cu(2,6\text{-}DMB)_2(2\text{-}Mepz)_2(H_2O)_2]$ (c), $[Cu(2,6\text{-}DMB)_2(2\text{-}Mepz)]$ (d), and $[Cu(2,6\text{-}DMB)_2(2\text{-}Mepz)_2]$ (e).

Examination of ESR and absorption data shows that $g_\parallel$ values $\leqslant 2.25$ are measured for $[Cu(2,6\text{-}DMB)_2(4\text{-}Etpy)_2]$, $[Cu(2,6\text{-}DMB)_2(2\text{-}Mepz)_2]$ and $[Cu(2,6\text{-}DMB)_2(py)_2]$, indicating that for all three complexes a nearly planar CuN_2O_2 chromophore is tenable. Support for this view is given by the electronic spectra, which show similar features consisting of bands at $17.2\text{–}17.8 \times 10^3\,cm^{-1}$ accompanied by shoulders at lower energy values, as is typical of strongly distorted tetragonal chromophores.

The higher $g_\parallel$ (or g_1) values observed for $[Cu(2,6\text{-}DMB)_2(2\text{-}Mepz)_2(H_2O)_2]$ and $[Cu(2,6\text{-}DMB)_2(pz)(H_2O)_2]$ are consistent with tetragonally distorted octahedral metal coordination due to axial binding of water molecules. Accordingly, broad absorptions, shifted toward lower energy values, are observed in the electronic spectra. The hypothesis is supported by a dehydration study. In particular, the $g_\parallel$ value (2.26) and the energy of the absorption maximum for the anhydrous complex $[Cu(2,6\text{-}DMB)_2(pz)]$ are comparable to those of the compound $[Cu(2,6\text{-}DMB)_2(py)_2]$. This finding confirms the bridging behaviour of pyrazine.

As already noted, $[Cu(2,6\text{-}DMB)_2(Im)_2(H_2O)_2]\cdot H_2O$ does not exhibit a resolved ESR spectrum. However, the absorption maximum is observed at energy values which are intermediate between those of, *e.g.*, $[Cu(2,6\text{-}DMB)_2(2\text{-}Mepz)_2(H_2O)_2]$ and $[Cu(2,6\text{-}DMB)_2(2\text{-}Mepz)_2]$. Therefore, the presence of axially bound water molecules is suggested also for the bis-adduct of imidazole. Accordingly, the dehydrated complex exhibits ESR and absorption features resembling those of nearly planar $[Cu(2,6\text{-}DMB)_2B_2]$ compounds, including $[Cu(2,6\text{-}DMB)_2(1\text{-}MeIm)_2]$.

$[Cu(2,6\text{-}DMB)_2(2\text{-}Phim)_2]\cdot 1.5\,MeOH$ shows a $g_{\parallel}$ value of *ca* 2.33 and a very broad electronic absorption centred at *ca* $13.7 \times 10^3\,cm^{-1}$. This, however, cannot be considered supportive of axial coordination of MeOH, because the removal of solvent does not result in any significant spectral change. Thus the ESR parameters and the low energy value of the absorption maximum could be better explained by a *pseudo*-tetrahedral distortion of the CuN_2O_2 chromophore or by bidentate asymmetric binding of the carboxylate group. Since the IR results (see later) exclude bidentate coordination for the carboxyl groups, the first hypothesis is more tenable.

The $[Cu(2,6\text{-}DMB)_2(2\text{-}Mepz)]$ complex has both $g_{\parallel}$ and absorption energy values which are higher and lower, respectively, than those for nearly planar anydrous bis-adducts. Bridging bidentate behaviour of the base, leading to significant distortion of the resulting CuN_2O_2 coordination, is probable also in this case.

TABLE III
Characteristic vibrational spectral data (cm^{-1}).

Compound	ν_{OH}(H_2O or MeOH)	ν_{NH}	ν_{as}(OCO)	ν_s(OCO)	$\Delta\nu$(OCO)	ν(M–N)
$[Cu_2(2,6\text{-}DMB)_4(H_2O)_2]$			1618s	1416s	202	
$[Cu_2(2,6\text{-}DMB)_2(O_2CCH_3)_2(H_2O)_2]$			1628s	1427s	201	
$[Cu(2,6\text{-}DMB)_2(py)_2]$			1585s	1381s	204	267s
$[Cu(2,6\text{-}DMB)_2(4\text{-}Etpy)_2]$			1616vs	1360m	256	285s
$[Cu(2,6\text{-}DMB)_2(Im)_2(H_2O)_2]\cdot H_2O$	3540m, 3400b	3030[a]	1585s	1377sb	208	256s
$[Cu(2,6\text{-}DMB)_2(1\text{-}Meim)_2]$			1614vs	1360m	254	246m
$[Cu(2,6\text{-}DMB)_2(pz)(H_2O)_2]$	3510mb		1578s	1393m	185	246m
$[Cu(2,6\text{-}DMB)_2(2\text{-}Mepz)_2(H_2O)_2]$	3380mb		1567s	1394s	173	247m
$[Cu(2,6\text{-}DMB)_2(2\text{-}Mepz)]$			1608mb	1360mb	248	252m, 230m
$[Cu(2,6\text{-}DMB)_2(2\text{-}Mepz)_2]$			1617s	1361s	256	276m, 245m
$[Cu(2,6\text{-}DMB)_2(2\text{-}Phim)_2]\cdot 1.5\,MeOH$	3430b	3300wb[a]	1614mb	1352mb	262	297s, 245m
$[Cu_2(2,6\text{-}DMB)_2(CH_3COO)_2(2\text{-}Phim)_2]$		3140w	1623vs	1410m	213	270m
$Na(2,6\text{-}DMB)\cdot 0.25H_2O$			1619s	1417s	202	

[a] Free ligand: Im, 3020b, 2-Phim 3140w.

Vibrational Spectra

Vibrational IR and far-IR data are listed in Table III. The main conclusions may be summarized a follows. The $\Delta(\nu_{as}-\nu_s)$ values measured for the carboxylate groups are invariably consistent with monodentate coordination, the slight decrease observed for the hydrated complexes being attributable to hydrogen-bonding interactions with water. In the 4000–3000 cm^{-1} range, OH (water or methanol) and NH (imidazole) stretches are observed. The NH stretches in the complexes of 2-phenylimidazole are observed at wavenumber values higher than those of the free base, thus ruling out the involvement of NH metal coordination. The bands are not significantly shifted in the imidazole adduct, suggesting that in this complex the NH groups take part in hydrogen bonding. The coordination of the base molecules to the metal ion is in all cases evidenced by Cu–N stretching bands in the 300–200 $\mathrm{cm^{-1}}$ range.[13]

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