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Synthesis and Characterization of Binuclear Complexes and their Catalytic Activity on the Oxidation of Catechol

U. RUSSO, M. VIDALI, B. ZARLI

Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Università di Padova, Padua, Italy

R. PURRELLO and G. MACCARRONE

Dipartimento di Scienze Chimiche, Università di Catania, Catania, Italy

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Metal ions of the first transition series such as Mn(II), Co(II), Fe(III), Cu(II), and some of their complexes are well known catalysts in the oxidation of catechols to orthoquinones by molecular oxygen [1]. As the reaction rates are dependent on the dioxygen concentration in these systems, an intermediate ternary dioxygen complex has been postulated, in which the electron transfer from the coordinated catecholate anion to the coordinated oxygen molecule occurs in successive one electron steps. Some of these systems, which have also been reported to effect the oxidative cleavage of catechol [2–5] are mimetic of the reactions that take place in the presence of catechol 1,2-dioxygenase and protocatechinate 3,4-dioxygenase enzymes. In these biological systems the proposed mechanism of oxygen incorporation involves a substrate activation by a ferric site [7–9]. This system is well studied and has been proved to give various products in both enzymatic and non-enzymatic reactions [10]. The catechol is initially bonded to the iron center [10] and subsequently oxidized. Comprehensive reviews on the role of the ferric ion in dioxygenase have been published [11, 12].

Weller and Weser reported on an interesting system consisting of an Fe(III) nitrilotriacetate complex, Fe(NTA), that is active in organic and borate buffer solutions [6]. Over a period of days, 3,5-di-terbutyl-5-(carboxymethyl)-2-furanone has been isolated from the oxidation reaction of 3,5-di-terbutyl catechol.

We have tried the same oxidative reaction by utilizing the binuclear iron(III) complex of (1-oxy-2,6-di(*N,N*-biscarboxymethyl)amino-methyl)4-chlorobenzol, $Fe_2L(OH)(H_2O)_2$. The iron environment in this binuclear complex is very similar to that of Fe(NTA) utilized by Weller and Weser and so the same catalytic behaviour in the catechol oxidation is expected. For comparison, the binuclear complexes of Co(II), Mn(II), and Cu(II) were prepared and tested in the same reaction.

Experimental

The ligand (1-oxy-2,6-di[(*N,N*-biscarboxymethyl)-aminomethyl]-4-chlorobenzol, (H_5L), was prepared according to literature methods [13] and its purity was determined by elemental analysis, melting point, and thin layer chromatography.

Preparation of the Binuclear Complexes

1 mmol of the ligand was suspended in methanol and the stoichiometric amount of LiOH was added; the resulting solution was poured into a methanolic solution of the appropriate metal chloride or perchlorate salt. The mixture was stirred at room temperature for 4 h and then the solvent was partially evaporated under reduced pressure. A microcrystalline powder was so obtained; it was filtered, washed with methanol and diethyl ether, and dried under vacuum over P_2O_5.

Oxidative Reactions

20 ml of a methanolic solution of 3,5-di-terbutyl-catechol (1 mmol) were added to a borate buffer solution (10 ml, pH = 8.5) of the metal complex (0.1 mmol) at 20 °C. The resulting mixture was stirred under an oxygen atmosphere (760 torr) for several days, until the color change ended. The reaction was followed by thin layer chromatography. A colored precipitate was formed; it was collected and identified by elemental analysis and physicochemical measurements. Removal of the methanol from the filtrate was followed by extraction in chloroform from a basic and then an acidic solution. When necessary, the products were separated by chromatography on silica with $CHCl_3$ as eluent.

Results and Discussion

The reaction of H_5L in methanol with the appropriate metal salt in molar ratio 1:2 gave the complexes reported in Table I as microcrystalline powders. They are soluble in coordinating solvents and practically insoluble in chloroform, methylene chloride, and acetonitrile. The infrared spectra, obtained as KBr pellets, are, as expected, characterized by the presence of a strong, very broad band ranging from 3600 to 3200 cm^{-1} due to the stretching of coordinated water. The band found at 2980 cm^{-1} is typical of the CH_2 stretching modes. Two strong absorptions have been found at 1600 and 1400 cm^{-1} which are attributed to the asymmetric and symmetric stretching vibrations of the coordinated carboxylic groups respectively. Moreover the spectrum of the iron(III) complex shows a band

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TABLE I. Elemental Analyses (%) and Magnetic Moments (BM)

Compound	C		H		N		H_2O		Metal		μ_{eff} (297 K)
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	
$Fe_2LOH(H_2O)_2$	33.22	33.54	3.31	3.62	4.84	4.99	6.22	6.53	19.31	19.07	4.17
$Cu_2L(H_2O)_2$	33.26	33.62	3.31	3.56	4.84	4.90	6.23	6.48	21.99	21.70	1.66
$Co_2L(H_2O)_2$	33.79	33.40	3.37	3.52	4.93	4.69	6.33	6.50	19.70	19.43	4.40
$Mn_2L(H_2O)_2$	34.27	34.58	3.41	3.68	4.99	4.85	6.42	6.60	19.59	19.38	4.85

at 550 cm^{-1} attributable to the Fe–O stretching vibration of the bridging hydroxyl group.

The electronic spectrum of the iron(III) compound, obtained in water solution, shows a band at 514 nm that is shifted to 503 nm in nujol mull. It has been assigned to a charge transfer or an intraligand transition. An analogous electronic spectrum, at least in nujol mull, has been obtained for the mononuclear complex. The magnetic moment (see Table I) is much lower than that expected from the spin-only value for a high-spin iron(III) complex. This indicates strong coupling interactions between the two ions by means of the hydroxyl and the phenate group. Consequently for this compound we propose a hexacoordinate structure around the iron ions as shown in Fig. 1. While this work was in progress, a binuclear iron(III) complex with a similar ligand was reported in the literature [14]; its X-ray crystal structure supports our proposal.

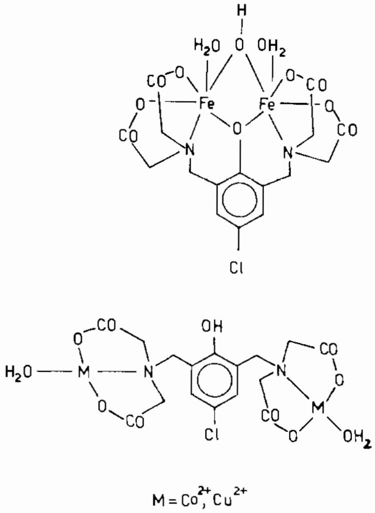


Fig. 1.

The magnetic moment at room temperature for the copper(II) complex is only slightly lower than the spin-only value, and it may not be due to a magnetic interaction between the two metal ions. The value of the magnetic moment for the cobalt(II) complex is very close to that expected for tetrahedral high-spin compounds in which the metal ions are diluted [15]. The magnetic moment of the manganese(II) complex presents the same value as has been found for the Schiff base [15] where a magnetic interaction between the metal ions is proposed. The infrared spectra of these compounds are identical to that of the iron(III) complex, but the absorption due to the M–O stretching that is not now found. On this basis a tetrahedral coordination geometry may be proposed for the copper(II) and cobalt(II) complexes (see Fig. 1). For the manganese(II) complex, in which a spin interaction seems to be present, a different structure around the metal ion may be suggested. The metal ion is octahedrally coordinated in a polymeric chain formed by bridging carboxylic oxygens. The electronic spectra of these complexes recorded in aqueous solutions show bands suggesting that an octahedral environment for the metal centers is present at least when using very coordinating solvents.

Oxidative Reactions

Iron(III) nitrilotriacetate, (Fe(NTA)), that has a coordination geometry similar to that proposed for our binuclear iron(III) complex, shows catechol cleavage activity in organic buffer solution [6]. So the study of the catalytic activity of our compound in the oxidation of 3,5-di-terbutylcatechol (DTBC) seemed to be worthwhile. The same reaction conditions as those reported for Fe(NTA) have been utilized. Typical conditions and results are reported in Table II. The results indicate that this compound is not selective and that the catechol is preferentially oxidized to quinone instead of undergoing a catechol cleavage.

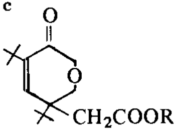
For comparison, the catalytic activity of the copper(II), manganese(II), and cobalt(II) complexes was tested (see Table II) and only 3,5-di-terbutylquinone has been isolated from the reaction mixture.

Work is in progress to improve the understanding of the electronic and catalytic properties of these and other omo- and etero-binuclear complexes.

TABLE II. Oxidation of Di-t-butylcatechol Catalyzed by Binuclear Complexes

Complex	Amount of catalyst (%)	Solvent[a]	Time (days)	Conversion[b] (%)	Products (%)	
					DTBQ	Lactone[c]
$Fe_2LOH(H_2O)_2$	10	DMF	6	100	85	15
$Fe_2LOH(H_2O)_2$	1	DMF	7	100	87	13
$Fe_2LOH(H_2O)_2$	10	MeOH	5	100	82	18
$Fe_2LOH(H_2O)_2$	1	MeOH	6	100	84	16
$Co_2L(H_2O)_2$	1	MeOH	4	100	100	
$Cu_2L(H_2O)_2$	1	MeOH	5	100	100	
$Mn_2L(H_2O)_2$	1	MeOH	5	100	100	

[a] 1 Part aqueous 0.6 M borate buffer pH 8.5, 2 parts of MeOH or DMF. [b] Based on original DTBC identification. [c]



R = H. ^{1}H NMR ($CDCl_3$): 0.95 δ (3H), 1.19 δ (9H), 2.76 δ (1H), 2.91 δ (1H), 6.91 δ (1H), 8.10 δ (1H). R = CH_3. ^{1}H NMR ($CDCl_3$): 0.95 δ (9H), 1.20 δ (9H), 2.80 δ (1H), 2.89 δ (1H), 3.95 δ (3H), 6.94 δ (1H).

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