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Synthesis, Characterization and Catalytic Properties of Mononuclear and Dinuclear Complexes of Uranyl(VI), Copper(II) and Nickel(II) with Compartmental Schiff Bases Derived from 2,6-Diformyl-4-chlorophenol and Polyamines

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Abstract

Mononuclear, homobinuclear and heterobinuclear complexes of copper(II), nickel(II) and uranyl(VI) with acyclic and symmetric and/or asymmetric cyclic ligands derived from 2,6-diformyl-4-chlorophenol and polyamines of the type $NH_2-(CH_2)_2-X-(CH_2)_2-NH_2$ and/or ethylenediamine are reported together with their physico-chemical properties and catalytic activity in the oxidation of 3,5-di-t-butylcatechol to 3,5-di-t-butylquinone.

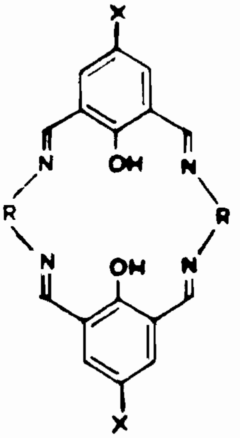
Coordination site change and transmetallation reactions have also been investigated by X-ray crystallography and scanning electron microprobe techniques.

Introduction

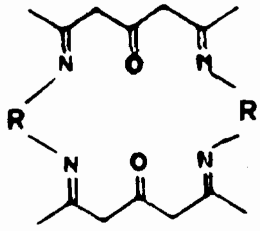
The role of multimetallic species is well known in a variety of metalloenzymes and in chemical catalysis. Many theoretical and experimental studies have been carried out in these fields [1–13].

Particular interest has been devoted to the synthesis and characterization of heterodinuclear compounds; generally these mixed-metal complexes have been prepared by using binucleating acyclic ligands of the type I–III which contain two different coordination sites and can thus link one metal ion in the inner N_2O_2 and the second in the outer O_2O_2 site [14–20].

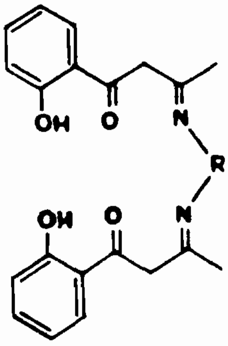
Other types of ligands, the macrocycles IV and V can simultaneously coordinate two metal ions in their two equivalent N_2O_2 coordination sites. With these



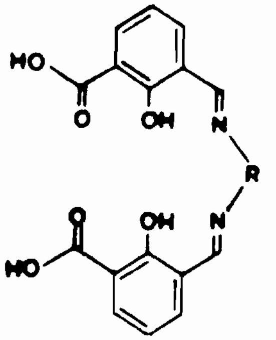
IV



V



I



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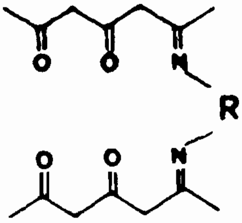

III

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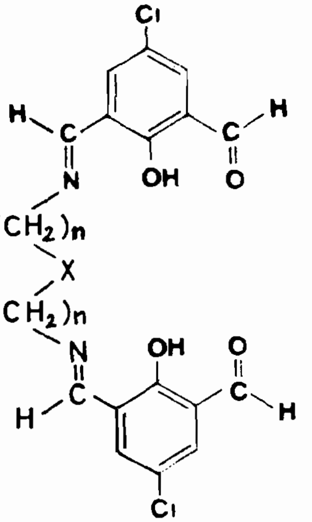
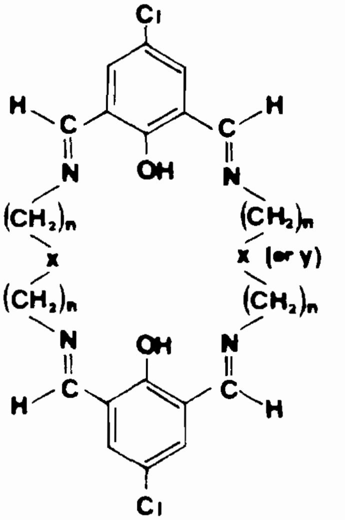
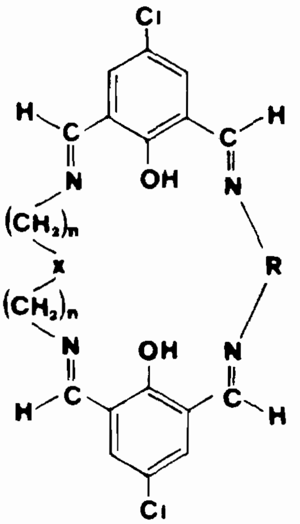


VI



VII
n = VII



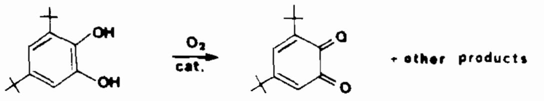
VIII

Acyclic ligands	Cyclic ligands	
	Symmetric	Asymmetric
H_2L_a: X = NH	H_2L_c: X = Y = NH	H_2L_e:X = NH, Y = S
H_2L_b: X = S	H_2L_d: X = Y = S	H_2L_f: X = NH
		H_2L_g: X = S

ligands homodinuclear complexes have easily been obtained [14, 15, 21] and heterobinuclear species have also been synthesized, by employing particular experimental conditions [22].

More recently we have introduced a facultative fifth donor atom into the chain R and we have successfully prepared acyclic and symmetric and/or asymmetric cyclic ligands **VI–VIII** and the related uranyl(VI), copper(II) and nickel(II) mononuclear and dinuclear complexes [23].

In the present paper we have extended these investigations to the synthesis and characterization of heterodinuclear complexes and to a deeper knowledge of their properties and catalytic activity in the oxidation reaction of 3,5-di-t-butylcatechol (3,5-DTBC) to 3,5-di-t-butylquinone (3,5-DTBQ).



The above ligands, having two similar or dissimilar compartments in close proximity, can link two metal ions in an identical or a different coordination mode.

In addition they offer the possibility for the metal ion in the mononuclear complexes to change the coordination site; a transmetallation reaction

$$M_aL + M_bCl_2 \longrightarrow M_aM_bLCl_2 \longrightarrow M_bL + M_aCl_2$$

L = acyclic or cyclic ligand

via the preliminary formation of a heterodinuclear complex can thus occur.

The present work also reports the results obtained in the coordination site change and in the transmetallation reactions.

Experimental

2,6-Diformyl-4-chlorophenol was prepared by literature methods [24]; ethylenediamine, 1,5-diamino-3-azapentane and 1,5-diamino-3-thiapentane are commercial products (K & K) and were used without further purifications.

The ligands H_2L_a, H_2L_b, H_2L_c, H_2L_d, H_2L_e, H_2L_f, H_2L_g and the mononuclear acyclic complexes NiL_a, NiL_b, UO_2L_a, UO_2L_b, CuL_b, were prepared according to the literature [23].

Preparation of Mononuclear Cyclic Complexes

1. With symmetric cyclic ligands

$UO_2L_c \cdot H_2O$. To an acetonitrile solution (30 ml) of UO_2L_a (200 mg, 0.28 mmol), 1,5-diamino-3-azapentane (30 mg, 0.28 mmol) dissolved in acetonitrile (20 ml) was added dropwise at room temperature. Within 2 days an orange precipitate was collected by filtration and dried *in vacuo*.

$UO_2L_d \cdot H_2O$. Method A. To a refluxing chloroform solution (30 ml) of H_2L_d (268 mg, 0.5 mmol), $UO_2(OAc)_2 \cdot 4H_2O$ (212 mg, 0.5 mmol) dissolved in methanol (20 ml) was added. The resulting red–brown solution was refluxed for 1 h, then evaporated to dryness and the residue was treated with chloroform and refluxed for 3 h. The red–brown precipitate obtained on cooling was filtered, washed with methanol and dried *in vacuo*. Method B. The preparation is identical to that of method A except that LiOH (24 mg, 1 mmol) was added to the solution of H_2L_d.

2. With asymmetric cyclic ligands

The complexes UO_2L_f and $UO_2L_e \cdot H_2O$ were prepared by the same procedure as UO_2L_c, employing ethylenediamine (17 mg, 0.28 mmol) or 1,5-diaminio-3-thiapentane (34 mg, 0.28 mmol), instead of 1,5-diamino-3-azapentane.

Preparation of Binuclear Complexes

1. With acyclic ligands

$NiCuL_aCl_2 \cdot 4H_2O$. To a stirring solution of $CuCl_2 \cdot 2H_2O$ (45 mg, 0.3 mmol) in methanol (50 ml), NiL_a (150 mg, 0.3 mmol) was added at room temperature. The yellow suspension turns green; after 2 h the solvent was partially evaporated and diethylether was added to the solution. The green precipitate obtained was collected by filtration, washed with diethylether and dried *in vacuo*.

$NiCuL_b(OAc)_2 \cdot 3H_2O$. To a yellow suspension of NiL_b (509 mg, 1 mmol) in chloroform (50 ml), $Cu(OAc)_2 \cdot H_2O$ (200 mg, 1 mmol) dissolved in methanol (30 ml) was added dropwise. The green suspension obtained was stirred overnight at room temperature; the solvent was evaporated to dryness and the residue was treated with chloroform (50 ml). To the resulting bright green solution, diethylether was added and the green precipitate obtained was filtered, washed with diethylether and dried *in vacuo*.

$NiCuL_bCl_2 \cdot H_2O$. To a stirring solution of $CuCl_2 \cdot 2H_2O$ (170 mg, 0.69 mmol) in methanol (30 ml), NiL_b (350 mg, 0.69 mmol) was added. The green precipitate obtained was collected, washed with diethylether and dried *in vacuo*.

$CuNiL_b(OAc)_2 \cdot 2H_2O$. To a stirring suspension of CuL_b (300 mg, 0.58 mmol) in methanol (50 ml), $Ni(OAc)_2 \cdot 4H_2O$ (145 mg, 0.58 mmol) was added. The resulting solution was stirred for 2 h; the solvent was then evaporated to dryness and the residue was dissolved with chloroform. The green precipitate obtained by addition of diethylether was filtered, washed with diethylether and dried *in vacuo*.

$UO_2ML_bCl_2 \cdot 2H_2O$ ($M = Cu^{2+}$, Ni^{2+}). To an orange solution of UO_2L_b (183 mg, 0.25 mmol) in chloroform (50 ml), $CuCl_2 \cdot 2H_2O$ (45 mg, 0.25 mmol) or $NiCl_2 \cdot 6H_2O$ (62 mg, 0.25 mmol) in methanol (30 ml) was added; immediately the solution turns green (for copper) or yellow (for nickel) and within a few minutes a precipitate had formed. The suspension was evaporated to dryness and the residue was stirred with chloroform (100 ml) overnight. The precipitate obtained (green for copper(II) or yellow for nickel(II)) was collected by filtration and dried *in vacuo*.

2. With asymmetric cyclic ligands

$NiCuL_f(OAc)_2 \cdot 3H_2O$. To a yellow suspension of NiL_a (248 mg, 0.5 mmol) in methanol (30 ml), $Cu(OAc)_2 \cdot H_2O$ (100 mg, 0.5 mmol) dissolved in methanol (20 ml) was added. To the green suspension obtained, ethylenediamine (30 mg, 0.5 mmol) in methanol (10 ml) was added; the suspension was stirred overnight; then the solvent was evaporated to dryness and the residue was dissolved with dichloromethane. The green precipitate obtained by addition of diethylether was collected by filtration and dried *in vacuo*.

$CuNiL_g(OAc)_2 \cdot 3H_2O$. To a stirring solution of CuL_b (150 mg, 0.3 mmol) in chloroform (70 ml), $Ni(OAc)_2 \cdot 4H_2O$ (74 mg, 0.3 mmol) in methanol (20 ml) was added. The solution was refluxed for 1h, then ethylenediamine (20 mg, 0.33 mmol) in methanol (10 ml) was added. After 30 min the solution was evaporated to dryness and the product was dissolved with chloroform. By addition of diethylether a green precipitate was obtained, collected by filtration and dried *in vacuo*.

3. With cyclic symmetric ligands

$NiCuL_dCl_2 \cdot H_2O$. To a stirring solution of $NiCuL_bCl_2$ (200 mg, 0.3 mmol) in methanol (15 ml), 1,5-diamino-3-thiapentane (36 mg, 0.3 mmol) in methanol (20 ml) was added. Within 2 h a green precipitate was formed. The product was collected by filtration, washed with diethylether and dried *in vacuo*.

$CuNiL_d(OAc)_2 \cdot 4H_2O$. To a solution of $CuNiL_b(OAc)_2$ (207 mg, 0.3 mmol) in chloroform (70 ml), 1,5-diamino-3-thiapentane (36 mg, 0.3 mmol) in methanol (20 ml) was added dropwise with stirring. After 2 h the solvent was evaporated to dryness and the residue was dissolved with chloroform. To this solution diethylether was added and the green precipitate obtained was washed with diethylether and dried *in vacuo*.

Oxidation Tests

A chloroform or methanol solution (40 ml) of 3,5 DTBC (1 mmol) was added to a solution of the appropriate complex (0.01 mmol).

The resulting solution was kept at 18 °C in a round flask for 24 h. The presence of the quinone formed (3,5 DTBQ) was determined by thin layer chromatography (TLC) over silica gel plates, eluting with chloroform/methanol.

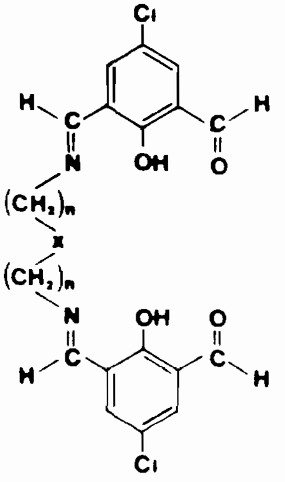
The yield of the quinone was determined by High Performance Liquid Chromatography on a Hewlett Packard 1090 model chromatographer equipped with a UV 600–220 nm detector. The column was Erbasil 10 μm (250 cm X 4.6 mm). The above reaction mixture was chromatographed in 75% chloroform and 25% methanol as eluent; detectors were set at 400 and 270 nm.

Physical Measurements

The IR spectra were carried out as KBr pellets by using a Perkin-Elmer 580B model Infrared Spectrophotometer. Electronic spectra were carried out, in dimethylsulphoxide solution, at room temperature by using a Cary 17D model Spectrophotometer. Magnetic susceptibilities were determined by the Faraday method at room temperature, by using an Oxford Instrument, the apparatus being calibrated with $HgCo(NCS)_4$ [25]. Diamagnetic corrections were carried out using Pascal's constants [26].

Metal ratios were conveniently determined by the integral counting of back scattered X-ray fluorescence radiation from a Philips SEM 505 Model scanning electron microscope equipped with an EDAX Model Data Station.

Samples, suitable for SEM analysis, were prepared by suspending the microcrystalline powders in petroleum ether 30–40%. Some drops of the resulting suspension were placed on a graphite plate and after evaporation of the solvent the samples were metallized with gold or graphite by using an Edward's S150B model sputter coater.



n = 2

IX

X-ray powder analysis was carried out on a Siemens 11 model diffractometer and the single crystal X-ray data were collected by a PW-1100 Philips diffractometer with monochromated Mo Kα radiation. Elemental analyses and infrared data of the prepared complexes are reported in Table I and Table II, respectively. Table III reports the electronic and magnetic data for the same compounds.

Results and Discussion

Although the acyclic Schiff base IX has two coordination sites, nickel(II), copper(II) and uranyl(VI) give rise to pure mononuclear complexes with the metal ion in the inner N_2XO_2 compartment.

In these complexes ambiguities remain about the coordination of the donor atom X of the ligand to copper(II) or nickel(II).

It was reported that the pentadentate Schiff base, bis-salicylidene-1,5-diimino-3-azapentane is unable, without strain, to act in monomeric species as quinquedentate ligand [27].

The paramagnetism of the nickel(II) complexes could, however, suggest a coordination of the five donor atoms of the site. These complexes are sparingly soluble in the common organic solvents, thus preventing correct measurements in solution. Their solubility is enhanced in coordinating solvents such as pyridine, but coordination of solvent molecules to the central metal ion can occur, especially when the samples are dissolved in hot pyridine to obtain crystals for an X-ray investigation.

Such an investigation [28] showed that NiL_b gives rise by this procedure to $NiL_b(py)_2$ which is a six-coordinate monomeric complex with Ni^{2+} in a slightly distorted octahedral symmetry as shown in Fig. 1. Two pyridine molecules occupy *cis*-positions while the thioetheric sulphur is not coordinated.

The equatorial pentacoordination geometry about the uranyl(VI) ion requires the formation of a U–X bond.

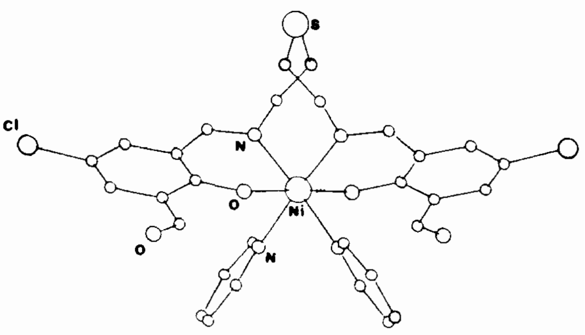
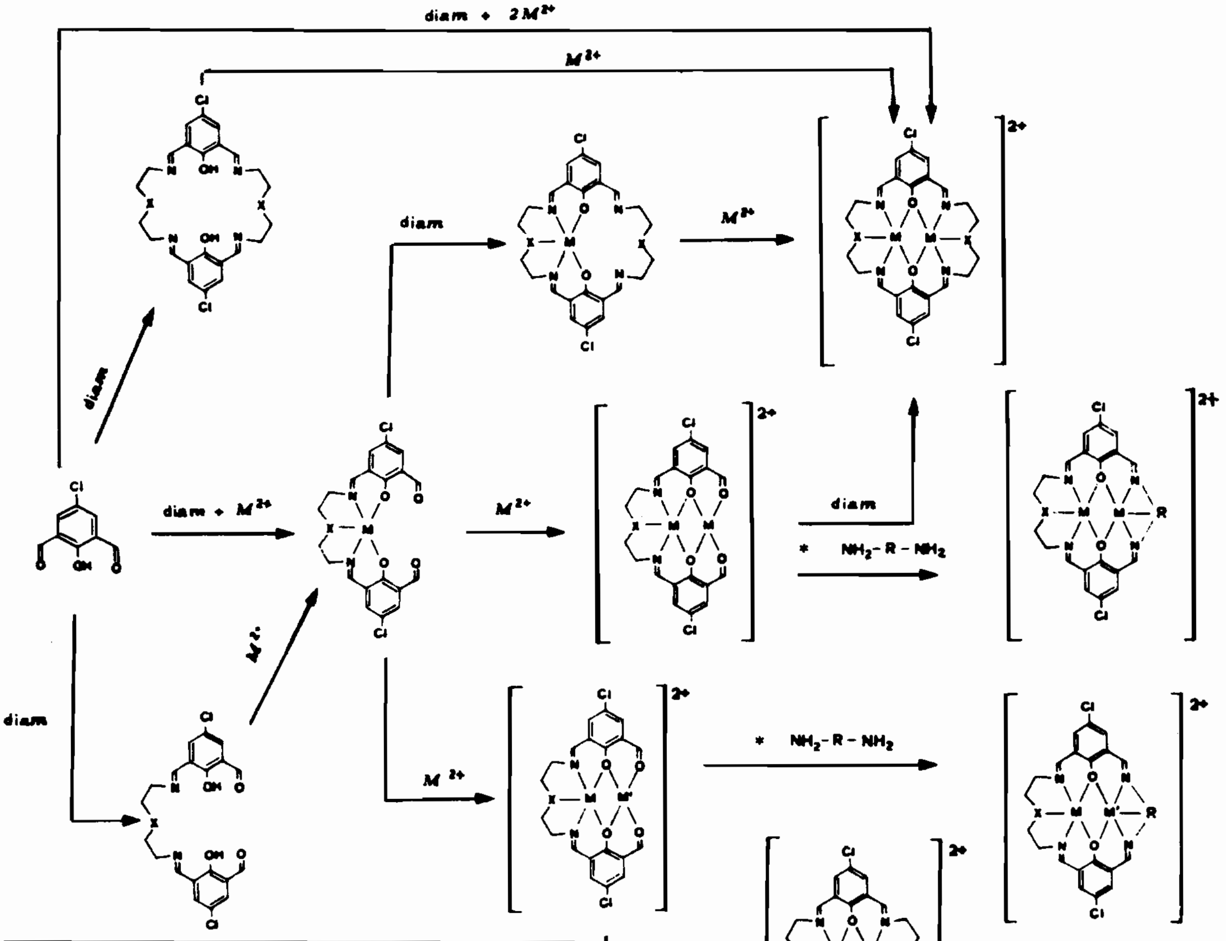


Fig. 1. The structure of $NiL_b(py)_2$.



diam = diamines	M^{2+}	M'^{2+}
NH_2–$(CH_2)_2$–NH–(CH_2)–NH_2	Cu^{2+}	Cu^{2+}
NH_2–$(CH_2)_2$–S–(CH_2)–NH_2	Ni^{2+}	Ni^{2+}
	UO_2^{2+}	

*Binuclear complexes with asymmetric cyclic ligands, where R = $-CH_2CH_2-$ or $-(CH_2)_2-S-(CH_2)_2-$ for diam = $-(CH_2)_2-NH-(CH_2)_2-$ and R = $-CH_2CH_2-$ or $-(CH_2)_2-NH-(CH_2)_2-$ for diam = $-(CH_2)_2-S-(CH_2)_2-$.

Scheme 1.

Scheme 1 reports the ligands and the complexes obtained by reaction of 2,6-diformyl-4-chlorophenol and the polyamines $NH_2-(CH_2)_2-X-(CH_2)_2-NH_2$ (X = NH, S) and $NH_2-(CH_2)_2-NH_2$, also in the presence of uranyl(VI) diacetate, copper(II) and nickel(II) diacetate or dichloride. In the symmetric cyclic mononuclear complexes, the metal ion occupies one of the two identical compartments; obviously the change from one coordination site to the other does not involve any variation in the physico-chemical properties of the complex. The difference in the coordination ability of the two compartments in the asymmetric cyclic ligands is not always so high as to make one chamber selective for a particular metal ion. Consequently in the related mononuclear complexes it becomes easy for the central metal ion to change the coordination chamber, this depending on the physico-chemical properties of the organic site and of the metal ion.

Magnetic measurements can evidence such a change when the two chambers offer the possibility of different spin states for the central metal ion. It has already been reported that the mononuclear nickel(II) complexes with the ligands H_2L_f and H_2L_g are a mixture of positional isomers. Infrared, electrochemical and X-ray powder data can give useful additional information.

In the two cyclic uranyl(VI) complexes, obtained by reaction of UO_2L_a with 1,5-diamino-3-thiapentane and UO_2L_b with 1,5-diamino-3-azapentane respectively, the UO_2^{2+} group had to occupy two different coordination chambers, with the consequent formation of two isomers.

The two complexes have, however, the same X-ray powder pattern which can be associated with the same site occupancy in the two samples. A scanning electron microscopy analysis shows a similar morphology. The infrared spectra of the two complexes are completely comparable; in particular the NH lies at 3217–3219 cm^{-1} in both spectra; in addition the electrochemical behaviour of the two samples is identical within experimental error [29]. We are inclined to believe, according to these results, that the same compound is formed in both reactions, the uranyl ion preferring the 'harder' N_3O_2 site instead of the 'softer' N_2SO_2 one. Thus, according to these suggestions, the uranyl(VI) ion also undergoes a coordination chamber change, as found for d-transtion metal ions [23].

Homodinuclear cyclic uranyl(VI) complexes, starting from the corresponding mononuclear analogues were not prepared; a second uranyl(VI) ion seems to be too large to enter into the second chamber when the first is occupied by one UO_2^{2+} group. On contrary this chamber can serve as a coordinating site for a second smaller ion such as nickel(II) and copper(II). Reaction of the cyclic mononuclear uranyl(VI) complexes with nickel(II) or copper(II) salts produces the heterodinuclear complexes.

The preparation of heterodinuclear M_a(II)M_b(II)L complexes with acyclic and cyclic ligands (H_2L) was not always completely successfull. As reported above the two chambers of the ligands are not selective enough to prevent a change of coordination site of the metal ions; as a consequence of this, positional heterodinuclear complexes and scrambling of the type

$$2[M_a(II)M_b(II)L]^{2+} \longrightarrow [M_a(II)M_a(II)L]^{2+} + [M_b(II)M_b(II)L]^{2+}$$

can be contemporarily obtained.

This difficulty was overcome by employing, in some cases, the following procedure: the addition of M_b(II) salts to suspensions of M_a(II)L in methanol resulted in the rapid complexation of M_b(II) to the vacant O_2O_2 site (for the acyclic complexes) and, eventually (for the preparation of the cyclic complex), by the subsequent addition of the polyamine.

Provided that the time in solution was short and the temperature was apparently too low to surmount the activation barrier for dissociation, little scrambling was observed, as already observed for similar systems [22].

A useful technique in characterizing these complexes was X-ray fluorescence spectroscopy. By integration of back-scattered X-rays using a scanning electron microscope, metal ratios were approximated and the sample homogeneity was confirmed.

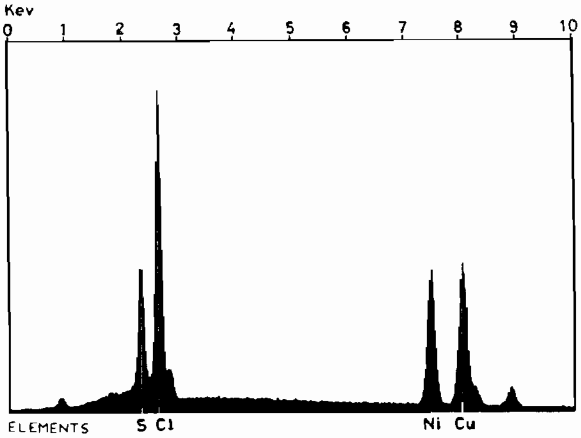


Fig. 2. X-ray fluorescence spectrum of $CuNiL_b(OAc)_2 \cdot 2H_2O$.

X-ray fluorescence spectroscopy enabled us to also check the S and Cl ratios in the compounds.

As an example in Fig. 2 the X-ray fluorescence spectrum of the complex $CuNiL_b(OAc)_2 \cdot 2H_2O$ is reported; the S, Cl, Ni, and Cu ratios are qualitatively 1:2:1:1. The quantitative analysis, which takes into account autoabsorption phenomena (ZAF corrections), also gives the same ratios 1:2:1:1 inside the standard error.

A photograph of $CuNiL_b(OAc)_2$ microcrystalline powders of about 1 micron size showing the homogeneity of the sample is reported in Fig. 3. On the other hand, X-ray fluorescence spectroscopy enabled us to discharge samples like that in Fig. 4, formulable, on the basis of elemental analyses, as $CuNiL_bCl_2 \cdot 3H_2O$ owing to different morphologies and different X-ray fluorescence patterns of the two species contained in the sample prepared (Fig. 5 and Fig. 6). Figure 5 shows the X-ray fluorescence spectrum of the globular particle, up in Fig. 4, which contains a high percentage of nickel with respect to the percentage of nickel with respect to the percentage of copper.

Fig. 3. A photograph of $CuNiL_b(OAc)_2 \cdot 2H_2O$ (microcrystalline powders of ≃1 micron size).

Fig. 4. A photograph of a sample formulable as $CuNiL_bCl_2 \cdot H_2O$ (the presence of two different compounds are easily detectable).

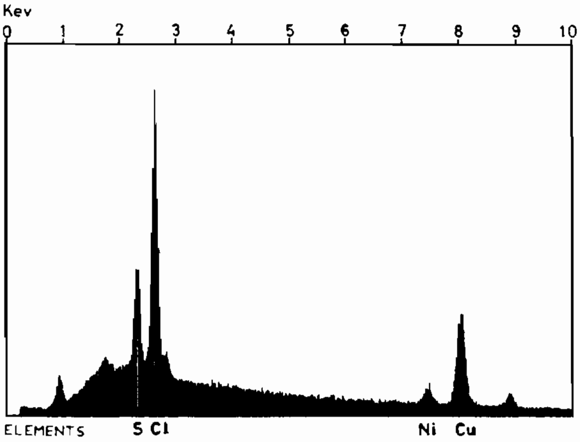


Fig. 6. X-ray fluorescence spectrum of the crystal in the lower part of Fig. 4.

Figure 6 shows the X-ray fluorescence spectrum of the crystal, down in Fig. 4, which contains a high percentage of copper with respect to the percentage of nickel. It is probably (on the basis of S, Cl, and Cu ratios) a crystal of CuL_b which did not react with $NiCl_2$ to form the heterobinuclear complex $CuNiL_bCl_2 \cdot 3H_2O$.

The complexes prepared are sparingly soluble in noncoordinating solvents; pyridine, dimethylsulphoxide or dimethylformamide must be employed to enhance their solubility. These solvents can however coordinate the central metal ions giving rise, sometime, to undesired products as found for $NiCuL_bCl_2 \cdot H_2O$.

This complex dissolved in dimethylformamide gave, after 3 weeks, deep green crystals containing only copper ions. The crystals were characterized as CuL_b. If we remember that for the preparation of $NiCuL_bCl_2 \cdot H_2O$ we started from the mononuclear complex NiL_b, the overall reaction is a transmetallation reaction, via the formation of a heterobinuclear species.

$$NiL_b + CuCl_2 \xrightarrow{\text{MeOH}} NiCuL_bCl_2 \xrightarrow{\text{dmf}} CuL_b + NiCl_2$$

Structural results based on single crystal X-ray diffraction data* show that CuL_b is formed by dinuclear molecules of formula $Cu_2(L_b)_2$.

Figure 7 shows a projection of the two molecules which form the asymmetric unit of the structure. Each molecule is a dinuclear complex in which the copper atoms are four coordinate.

The overall configuration is the same in the two molecules and their structural details are comparable. The coordination geometry is not the same for all copper atoms: one copper atom in each unit, namely, Cu(1) in molecule **A** and Cu(3) in molecule **B** can be described as distorted tetrahedral, which is a rather common feature in copper(II) complexes; the other copper atoms, Cu(2) in **A** and Cu(4) in **B** being intermediate between the distorted tetrahedral and the square planar geometry. In fact, bond angles reported in Table IV show that, while O–Cu–O angles for the four copper atoms are all comprised in the range 154–158°, the N–Cu(2)–N and N–Cu(4)–N sequencies are quasi linear with angles of 174° and 178° respectively, while the corresponding values at Cu(1) and Cu(3) are 156° and 152°, according with their mentioned coordination geometry. In addition, Cu(2) and Cu(4) make relatively short contacts with S(2) (3.00 Å) and S(3) (2.90 Å), which approximately occupy the apex of a distorted square pyramid, as shown in Figs. 8 and 9.

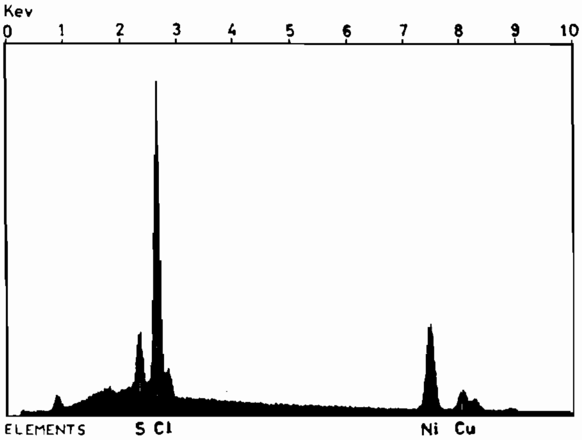


Fig. 5. X-ray fluorescence spectrum of the globular particle in the upper part of Fig. 4.

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*$Cu_2(L_b)_2$ is monoclinic, space group $P2_1/c$, with a = 16.076(5), b = 33.709(4), c = 20.094(5) Å, β = 91.34(5)°, V = 10 886 Å^3, D_c = 1.26 g cm^{-1} for Z = 4.

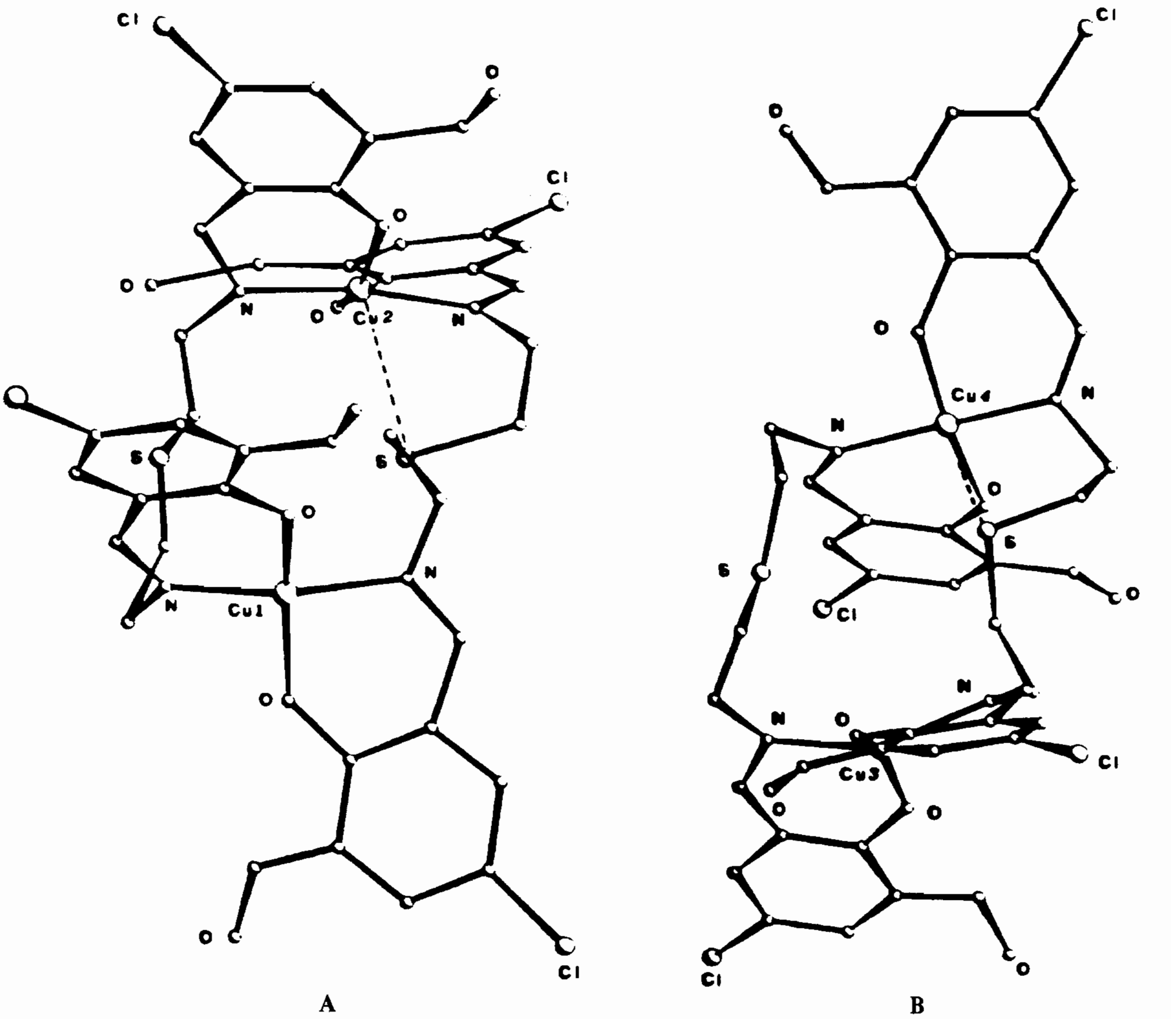

Fig. 7. Projection along [100] of the structure of Cu_2L_2. For clarity the diagrams of the two independent molecules (**A** and **B**) are separated.

TABLE I. Elemental Analyses of the Prepared Complexes

	Calculated			Found		
	C%	H%	N%	C%	H%	N%
$NiCuL_aCl_2 \cdot 4H_2O$	34.34	3.60	6.01	33.77	3.06	6.09
$UO_2CuL_bCl_2 \cdot 2H_2O$	26.94	2.26	3.14	26.69	2.53	3.80
$UO_2NiL_bCl_2 \cdot 2H_2O$	27.08	2.27	3.16	26.87	2.61	3.69
$NiCuL_b(OAc)_2 \cdot 3H_2O$	38.66	3.78	3.76	38.8	3.54	3.52
$NiCuL_bCl_2 \cdot H_2O$	36.26	2.74	4.23	36.94	3.00	4.48
$CuNiL_b(OAc)_2 \cdot 2H_2O$	39.61	3.60	3.85	39.17	3.61	3.03
$UO_2L_c \cdot H_2O$	36.51	3.58	10.64	36.16	3.35	10.58
$UO_2L_d \cdot H_2O$	35.00	3.18	6.80	35.01	2.96	6.52
$UO_2CuL_d(ClO_4)_2 \cdot 2ETOH$	29.04	3.11	4.84	29.57	3.05	5.35
$CuNiL_d(OAc)_2 \cdot 4H_2O$	39.66	4.52	6.61	39.69	4.13	6.69
$NiCuL_dCl_2 \cdot H_2O$	38.61	3.51	7.50	38.64	3.83	7.47
$UO_2L_e \cdot H_2O$	35.74	3.37	8.68	35.3	3.58	8.66
UO_2L_f	36.28	2.91	9.61	36.43	2.96	9.43
$NiCuL_f(OAc)_2 \cdot 3H_2O$	41.49	4.42	9.30	42.03	4.38	9.16
$CuNiL_g(OAc)_2 \cdot 3H_2O$	40.57	4.19	7.28	40.53	3.89	6.88

TABLE II. Infrared Data (cm^{-1}) for the Prepared Complexes

Compound	IR frequencies in the range 1700–1500 cm^{-1} assignable to C–O, C–N and C–C	Other characteristic bands
$NiCuL_aCl_2 \cdot 4H_2O$	1651b, 1545s	3253sh (ν N–H)
$UO_2CuL_bCl_2 \cdot 2H_2O$	1628b, 1550s	903s (ν O–U–O)
$UO_2NiL_bCl_2 \cdot 2H_2O$	1655b, 1540s	916s (ν O–U–O)
$NiCuL_b(OAc)_2 \cdot 3H_2O$	1636s, 1542s	1565s (ν as COO^-), 1418s (ν sym COO^-)
$NiCuL_bCl_2 \cdot H_2O$	1650b, 1544s	
$CuNiL_b(OAc)_2 \cdot 2H_2O$	1634s, 1556sh	1566s (ν as COO^-), 1422s (ν sym COO^-)
$UO_2L_c \cdot H_2O$	1631s, 1552s	895s (ν_3 O–U–O), 3248b (ν N–H)
$UO_2L_d \cdot H_2O$	1632s, 1552s	896s (ν_3 O–U–O)
$UO_2CuL_d(ClO_4)_2 \cdot 3EtOH$	1636s, 1554m	896s (ν_3 O–U–O), 1146s, 1120s, 1091s, 1112s (ν ClO_4^-)
$CuNiL_d(OAc)_2 \cdot 4H_2O$	1629s, 1547s	1567s (ν as COO^-), 1408s (ν sym COO^-)
$NiCuL_dCl_2 \cdot H_2O$	1632b, 1541s	
$UO_2L_e \cdot H_2O$	1635s, 1553s	892s (ν_3 O–U–O), 3219m (ν N–H)
UO_2L_f	1630s, 1553s	894s (ν_3 O–U–O), 3253b (ν N–H)
$NiCuL_f(OAc)_2 \cdot 3H_2O$	1647s, 1545s	1569b (ν as COO^-), 1408s (ν sym COO^-), 3278sh (N–H)
$CuNiL_g(OAc)_2 \cdot 3H_2O$	1634s, 1549s	1569s (ν as COO^-), 1408s (ν sym COO^-)

Once it was established that the prepared samples were not simply a mixture of the two homobinuclear complexes, the magnetic moments can give information about the interaction between the metal ions and about the structural configuration around them.

The effective magnetic moments per binuclear complex at room temperature (see Table III) are not considerably different than the 3.34 μ_B spin only value expected for a Cu^{II}–Ni^{II} complex with no exchange interaction present [30]. It may be suggested that the magnetic interaction in these systems is small. In addition all the binuclear complexes are paramagnetic, implying that Ni(II) is always in a non-square configuration.

Electronic spectra, carried out in dimethylsulphoxide, agree with the magnetic data; the binuclear complexes containing copper and/or nickel, show d–d bands (Table III) characteristic of a non-square geometry. In this coordinating solvent the copper(II) is very probably pentacoordinated and the nickel(II) octahedral.

The complexes containing uranyl(VI) show in the range 475–360 nm bands due also to charge transfer UO_2–L and to internal transitions of the O–U–O group.

The infrared spectra show in the range 1700–1500 cm^{-1}, bands due to C=O, C=N and C=C groups. In the acyclic complexes a lowering of the

TABLE III. Electronic (nm) and Magnetic (μ_B) Data of the Prepared Complexes

Complex	Electronic data in DMSO (nm)					Magnetic moment (μ_B)
$NiCuL_aCl_2 \cdot 4H_2O$	675	415	295sh			3.62
$UO_2CuL_bCl_2 \cdot 2H_2O$	665	460sh	410	300	280sh	1.80
$UO_2NiL_bCl_2 \cdot 2H_2O$	1000	430	300sh			3.03
$NiCuL_b(OAc)_2 \cdot 3H_2O$	690	495sh	405	300sh		3.9
$NiCuL_bCl_2 \cdot H_2O$	700	485sh	415	300sh	260sh	3.2
$CuNiL_b(OAc)_2 \cdot 2H_2O$	675	490	430sh	393	290sh	3.6
$UO_2L_c \cdot H_2O$	470sh	375				diam
$UO_2L_d \cdot H_2O$	465sh	450	360			diam
$CuNiL_d(OAc)_2 \cdot 4H_2O$	965	840	640	395	300sh	3.45
$NiCuL_dCl_2 \cdot H_2O$	940	860	650	408	305sh	3.16
$UO_2L_e \cdot H_2O$	475sh	400sh	377			diam
UO_2L_f	470sh	390sh	375			diam
$NiCuL_f(OAc)_2 \cdot 3H_2O$	965	870	600	395		3.48
$CuNiL_g(OAc)_2 \cdot 3H_2O$	970	850	620	395		3.53

TABLE IV. Selected Bond Lengths (A) and Angles (deg) for $Cu_2(L_b)_2$

Molecule A		Molecule B	
Cu(1)–O(1)	1.86(6)	Cu(3)–O(9)	1.91(4)
Cu(1)–O(2)	1.88(6)	Cu(3)–O(11)	1.88(4)
Cu(1)–N(1)	1.91(7)	Cu(3)–N(5)	2.00(5)
Cu(1)–N(2)	2.01(6)	Cu(3)–N(6)	2.03(6)
Cu(2)–O(5)	1.94(5)	Cu(4)–O(13)	1.96(5)
Cu(2)–O(7)	1.98(5)	Cu(4)–O(15)	1.95(5)
Cu(2)–N(3)	1.87(7)	Cu(4)–N(7)	1.95(6)
Cu(2)–N(4)	1.94(8)	Cu(4)–N(8)	1.95(4)
Cu(2)•••S(2)	3.00(3)	Cu(4)•••S(3)	2.90(3)
O(1)–Cu(1)–O(2)	158(2)	O(9)–Cu(3)–O(11)	154(2)
N(1)–Cu(1)–N(2)	156(3)	N(5)–Cu(3)–N(6)	152(2)
O(5)–Cu(2)–O(7)	156(2)	O(13)–Cu(4)–O(15)	154(2)
N(3)–Cu(2)–N(4)	174(3)	N(7)–Cu(4)–N(8)	178(2)

ν C=O, in comparison to the free ligands (Δν = 48–70 cm^{-1}), is attributable to the coordination of the second metal ion; in the cyclic complexes the ν C=N (often a doublet not well resolved) lies in the range 1629–1647 cm^{-1} as already found for the homodinuclear species [23], and analogously to those species the antisymmetric and symmetric stretchings of the acetate groups can be assigned at about 1569 and 1408 cm^{-1} respectively.

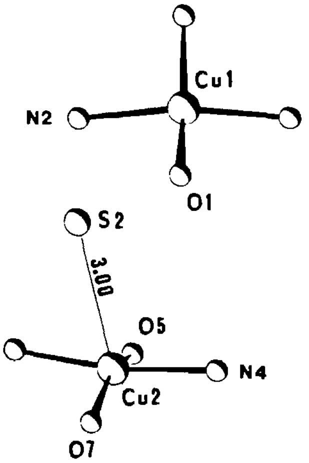

Fig. 8. Coordination geometries in molecule A. Projection along [100].

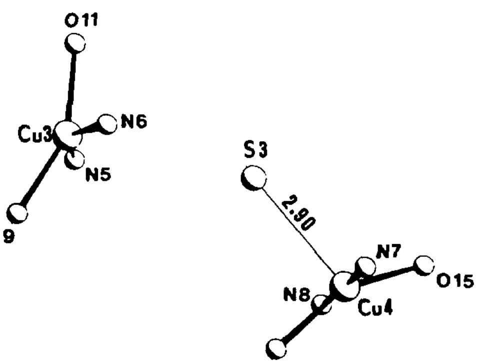

Fig. 9. Coordination geometries in molecule B. Projection along [010].

In this region other absorptions of the ligands are present; however a comparison with the analogous chloride and perchlorate complexes can strengthen the above assignments; the bands due to the ClO_4^- groups lie in the range 1146–1091 cm^{-1}.

The IR spectra suggest that the acetate groups are not completely involved in the coordination to the central metal ion as already reported [23]. It is however hazardous to use IR data alone for the assignment of a coordination behaviour of a ligand.

By considering that metal containing proteins and enzymes can catalyze the oxidation of particular organic substrates and that suitable complexes can be used as models which can imitate the special structure and the chemical behaviour of such proteins or enzymes, we have tested some of the mononuclear, homo- and heterodinuclear complexes prepared in the oxidation of 3,5-di-t-butylcathecol to 3,5-di-t-butylquinone (and to other oxidation products also).

The activity of these complexes was followed by HPLC, following the growth of 3,5-DTBQ and the contemporary decreasing of 3,5-DTBC. The complexes do not oxidize under a dinitrogen atmosphere but they act as catalysts in both dioxygen and air. The above results refer to reactions carried out in a dioxygen atmosphere; similar results can be obtained in air; there is obviously an increase in activity on going from air to a pure dioxygen atmosphere.

A comparison of the oxidation reaction for the complexes $Cu_2L_c(OAc)_2$, $Cu_2L_d(OAc)_2$, CuL_a, CuL_b, $CuUO_2L_d(ClO_4)_2$, $CuNiL_d(OAc)_2$ and NiL_b has shown that the major part of quinone is formed in 2–3 h and 80% of quinone is formed in 6–7 h. The oxidation was continued for 24 h.

The complexes can be divided into three categories $Cu_2L_c(OAc)_2$, $Cu_2L_d(OAc)_2$ and $CuNiL_d(OAc)_2$ (40% conversion in 24 h); CuL_a, CuL_b and $CuUO_2$-$L_d(ClO_4)_2$ (15–20% conversion in 24 h) and NiL_b (5–7%) conversion in 24 h.

The binuclear complex has an enhanced activity over the mononuclear complexes.

In a previous study [31] we carried out similar investigations by using a pyridine/chloroform solution. In a related series of experiments [32] it was found that the square planar configuration did not activate the oxidation; consequently it was suggested that the role of pyridine was to dissolve the complex but above all to allow the central metal ion (copper(II) in those experiments) to become pentacoordinated.

In our tests we have used only chloroform; it could be concluded that in this solvent the transition metal ion is, in the complexes examined, in a non-planar coordination.

The mononuclear NiL_b complex has the lowest conversion, while the heterodinuclear $CuUO_2L_b(ClO_4)_2$ has an oxidation behaviour close to that of CuL_a and CuL_b.

We have already found that mononuclear cobalt(II) complexes have little or no catalytic activity [31]; that of mononuclear nickel(II) complexes seems to be in between those of copper(II) and cobalt(II) analogues.

An unexpected result was obtained with the heterodinuclear $CuNiL_d(OAc)_2$ complex; its activity is similar if not better than that of the homodinuclear copper(II) complex.

Further systematic studies are in progress for a deeper knowledge of these oxidation processes.

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