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Studies on Copper(II) Complexes of *o*-Quinone Monooximes. 4.* Interaction between Aquobis(1,2-naphthoquinone 1-oximato)copper(II) and Lanthanide(III) Ions. New Heteropolynuclear Complexes Containing Cu^{II} and Ln^{III}

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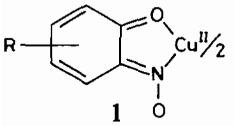
Abstract

By reacting aquobis(1,2-naphthoquinone 1-oximato)copper(II) [$Cu(nqo)_2 \cdot H_2O$] with lanthanide chlorides, new heteropolynuclear complexes containing both Cu^{II} and Ln^{III} ($Ln^{III} = La^{III}$, Nd^{III}) were obtained. The compounds have been characterized by elemental and thermogravimetric analysis, electron microprobe analysis, and electronic and vibrational spectral data. A different Cu^{II} complex, containing nqo ligands and ionic perchlorate but no lanthanide ions, was obtained by reaction of $Cu(nqo)_2 \cdot H_2O$ with lanthanide perchlorates.

Introduction

Interest in copper(II) complexes of *o*-quinone monooximes (generally referred to as $Cu(qo)_2$ (**1**)) is stimulated by their extensive reactivity, which is related to their Lewis acid behaviour [2]. In a previous report of this series, we studied the reactivity of bis(4-chloro-1,2-benzoquinone 2-oximato)-copper(II) ($Cu(Clqo)_2$ (**1a**)) with halides as Lewis bases [1]. Carrying out the reaction in methanol, the adduct $Cu(Clqo)_2 \cdot MeOH$ was obtained instead of or besides the expected halide adducts. Studying the role of the cation, it was observed that the methanol adduct is formed almost instantaneously, even at room temperature, in the presence of lanthanum chloride; a similar very fast process occurs with lanthanum perchlorate, while the perchlorates of other cations do not react. This behaviour has been explained as follows: $Cu(Clqo)_2$ is dimeric in solution [3] and in order to form monomeric adducts it is first necessary to break the intermolecular bridges between the copper centre of one unit and the oxygen atom of the next. This can be done either by Lewis bases as halides, which bind to Cu^{II} ions, or by hard Lewis acids such as lanthanide(III) ions, which coordinate the basic oxygen atoms of the ligands. It is therefore reasonable to suppose that in the course of the reaction intermediate heteropolynuclear complexes are formed in which $Cu(qo)_2$ acts as a ligand towards Ln^{III}.



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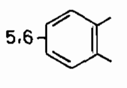
1a : R = 4-Cl

1b : R = 5,6-



The preparation of heteropolynuclear complexes and the study of their physicochemical properties, particularly the electronic and magnetic ones, is a research field of growing interest, owing to the possibility of industrial application of such materials. However, relatively few heteropolynuclear complexes containing both 'd' and 'f' metal ions have been reported [4].

Therefore we considered it worthwhile to investigate more fully the reactivity of $Cu(qo)_2$ with lanthanide chlorides and perchlorates, and succeeded in isolating heteropolynuclear complexes by reaction between $LnCl_3$ (Ln = La, Nd) and aquobis(1,2-naphthoquinone 1-oximato)copper(II) ($Cu(nqo)_2 \cdot H_2O$ (**1b**)). These are the first examples of heteropolynuclear complexes based on an *o*-quinone monooximate as ligand. The reaction of $Cu(nqo)_2 \cdot H_2O$ with lanthanide perchlorates instead gives a Cu^{II} polynuclear complex which does not contain lanthanide ions.

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*For Part 3, see ref. 1.

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Experimental

$Cu(nqo)_2 \cdot H_2O$, $Cu(Clqo)_2$, $K(Clqo) \cdot \frac{1}{2}H_2O$ and $La(nqo)_3$ were prepared as described in the literature [1, 3, 5].

K(nqo) was obtained as a green powder on neutralizing nqoH with KOH in methanol, refluxing for 1 h, and slowly evaporating the solvent at room temperature. *Anal.* Calc. for $C_{10}H_6KNO_2$: C, 56.85; H, 2.86; N, 6.63. Found: C, 57.30; H, 3.07; N, 6.50%.

The reactions between $Cu(nqo)_2 \cdot H_2O$ and lanthanide salts were carried out as follows: to 1 mmol of $Cu(nqo)_2 \cdot H_2O$ in 50 ml of methanol, 3 mmol of the lanthanide chloride or perchlorate in 20 ml of the same solvent were added; the mixture was refluxed for 1 h. All the products were obtained as powders by slow evaporation of the solvent at room temperature; they were washed with methanol and dried *in vacuo* at room temperature.

Reaction with Lanthanide Chlorides (Ln = La, Nd)

Products: red–brown powders formulated as $Cu_5Ln_2(nqo)_8Cl_8 \cdot 2(nqoH) \cdot 11H_2O$ (Ln = La, **2a**; Ln = Nd, **2b**). *Anal.* Calc. for $C_{100}H_{84}Cl_8Cu_5La_2N_{10}O_{31}$: C, 42.89; H, 3.03; N, 5.00; Cu, 11.35; La, 9.92; Cl, 10.13. Found: C, 43.01; H, 2.71; N, 5.00; Cu, 11.50; La, 10.00; Cl, 9.60%. *Anal.* Calc. for $C_{100}H_{84}Cl_8Cu_5N_{10}Nd_2O_{31}$: C, 42.72; H, 3.01; N, 4.98. Found: C, 42.48; H, 3.12; N, 5.02%*.

Reactions with Lanthanide Perchlorates (Ln = La, Nd, Sm, Er, Tb)

Product: dark red microcrystals formulated as $Cu_2(nqo)_3(ClO_4) \cdot \frac{1}{2}(nqoH) \cdot 2H_2O$ (**3**). *Anal.* Calc. for $C_{35}H_{25.5}ClCu_2N_{3.5}O_{13}$: C, 48.56; H, 2.97; N, 5.66; Cu, 14.68; Cl, 4.10. Found: C, 48.72; H, 2.72; N, 5.65; Cu, 14.32; Cl, 3.94%.

A Cambridge Steroscan 200 scanning electron microscope, an energy dispersion microanalysis unit (Link AN10000) equipped with a Si(Li) windowless detector (Link LZ5) and a back-scattered electron counter (Link) were employed in determination of the percentage of metal and chlorine in all the complexes obtained. Before analysis, samples and standard powders were pressed to pellets and uniformly metallized with graphite by using an E5000C-PS3 sputter coater. Electron microprobe analyses were carried out with ZAF4/FLS and ZAF PB correction methods (Link software). Microanalysis and back-scattered electron maps were also executed on sample powders, in order to verify the homogeneity of the products.

IR spectra were obtained on a Perkin-Elmer 1330 spectrophotometer on samples suspended in a KBr matrix, or Nujol mull. Electron absorption spectra were recorded with a Varian Cary 2300 spectrophotometer from 2000 to 200 nm; the solid state spectra were obtained by pasting the compounds with Nujol and spreading them on a strip of filter paper. Thermogravimetric measurements were carried out by means of the DuPont 1090 System under a dry N_2 flow of 4 l/h.

Magnetic susceptibilities were determined by the Faraday method at room temperature, the apparatus (Oxford Instruments) being calibrated with $HgCo(NCS)_4$ [6]. Diamagnetic corrections were carried out [7].

Results and Discussion

The reactions between $Cu(nqo)_2 \cdot H_2O$ and lanthanum and neodymium chlorides in methanol give isomorphous brown microcrystalline products which can be tentatively formulated as $Cu_5Ln_2(nqo)_8Cl_8 \cdot 2(nqoH) \cdot 11H_2O$ (Ln = La: **2a**; Ln = Nd: **2b**). The possibility that the products might be a mixture of various compounds instead of heteropolynuclear complexes containing both Cu^{II} and Ln^{III} ions has been ruled out by X-ray fluorescence spectroscopy. This technique, the use of which in the characterization of some polynuclear complexes has been recently described, enabled us to verify the homogeneity of the samples [4]. Unfortunately X-ray determination of the structure of these compounds was precluded by the very small size of the crystals obtained; however, some information can be deduced from thermogravimetric analysis and spectral data.

Water molecules are present both in the inner and in the outer coordination sphere; the dehydration in fact occurs through two consecutive processes, between 40 °C and 164 °C (total weight loss: **2a**, 7.2%; **2b**, 6.6%; calc. for $11H_2O$: **2a**, 7.1%; **2b**, 7.0%). The presence of two molecules of the ligand more loosely bonded than the others is deduced from the weight loss between 170 °C and 350 °C (Found: **2a**, 11.5%; **2b**, 13.5%. Calc. for 2(nqoH): **2a**, 12.4%, **2b**, 12.3%).

A detailed analysis of the IR spectra of nqoH and a series of its d-metal complexes has been reported in the literature [8]. The most characteristic features concern the C=O, C=N and N–O stretching frequencies, located in the regions of 1620–1590 cm^{-1}, 1580–1520 cm^{-1} and 1190–1065 cm^{-1}, respectively. In the present work the IR spectra of compounds **2a**, **2b** and **3** have been examined in comparison with the spectra of: (i) the parent compound $Cu(nqo)_2 \cdot H_2O$; (ii) the lanthanum salt $La(nqo)_3$; (iii) the

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*We considered the Cu, Nd and Cl analysis to be unnecessary because neodymium and lanthanum complexes are isomorphous, as demonstrated by X-ray powder diffraction patterns; moreover, their electronic and IR spectra are identical and their TGA are strictly similar.

TABLE I. Selected Vibration Frequencies (cm^{-1})

Compound	ν(C=O)	ν(C=N)	ν(N–O)
$K(Clqo)_2 \cdot \frac{1}{2}H_2O$	1617	1550	1110
$Cu(Clqo)_2$	1590	1520	1130
K(nqo)	1625	1570	1110
$La(nqo)_3$	1610	1550	1085
$Cu(nqo)_2 \cdot H_2O$	1600	1515	1185
Product **2a**	1610	1540	1180, 1090
Product **2b**	1610	1540	1180, 1090
Product **3**	1600	1550, 1520	1180

potassium salt K(nqo). Compounds $Cu(Clqo)_2$ and $K(Clqo) \cdot \frac{1}{2}H_2O$ have also been considered for comparison. Selected data are reported in Table I.

A striking similarity is observed between the spectra of K(nqo) and $La(nqo)_3$ which exhibit significant differences from the spectrum of the Cu^{II} complex. In going from K(nqo) and $La(nqo)_3$ to $Cu(nqo)_2 \cdot H_2O$, as well as from $K(Clqo) \cdot \frac{1}{2}H_2O$ to $Cu(Clqo)_2$, the C=O and C=N stretching vibrations are shifted to lower frequencies, while the N–O stretching is shifted to higher frequencies. This behaviour can be ascribed to a different linkage between the ligand and the metal ion. In $Cu(qo)_2$ the ligands are chelated to Cu^{II} through the quinonic oxygen and the oximic nitrogen (see 1), as demonstrated by the crystal structure of several $Cu(qo)_2$ adducts [9]. Instead, in the case of $K(Clqo) \cdot \frac{1}{2}H_2O$, whose structure has been recently determined by us, it has been found that the ligand behaves as a bridge, being linked to different potassium ions through the quinonic and the oximic oxygen atoms [9a].

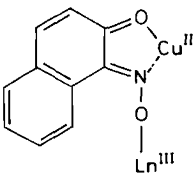
This behaviour is obviously related to the hard Lewis acid character of K^+ which, very likely, is bonded in the same way in K(nqo). In fact, the C=O, C=N and N–O stretching frequencies in $K(Clqo) \cdot \frac{1}{2}H_2O$ and in K(nqo) are very similar. Lanthanum ion is also a hard Lewis acid and the electronic spectra of $La(nqo)_3$ are strictly similar to those of K(nqo), both in solution and in the solid state [λ_{max} of $La(nqo)_3$ (in DMSO), 295, 360, 430 nm; (solid), 284, 398; λ_{max} of K(nqo) (in DMSO), 295, 360, 430 nm; (solid), 265, 385 nm]; therefore it is reasonable to suppose that in the two compounds the ligand-to-metal linkages are alike. Moreover, the low crystallinity of $La(nqo)_3$, demonstrated by its X-ray powder diffraction pattern, suggests a polymeric structure consistent with the bridging behaviour of the ligand. Such a structure would also allow the lanthanum ion to reach high coordination numbers, in spite of the rigidity and bulkiness of the nqo molecule.

Therefore we believe that the C=O and C=N stretching vibrations are found at higher frequencies in K(qo) and $La(nqo)_3$ than in $Cu(qo)_2$, because of the higher delocalization of electron density through the chelated ring in the last case. This should be reflected by C–O and C–N bond distances which should be longer in chelated compounds. Such a difference in bond lengths is actually observed both between $Cu(Clqo)_2$ and $K(Clqo) \cdot \frac{1}{2}H_2O$ [9a] and between chelated (*syn*) [10] and non-chelated (*anti*) [11] *o*-quinone monooximes.

The shift to higher frequencies of the N–O stretching in going from K(nqo) and $La(nqo)_3$ to $Cu(nqo)_2$, as well as from $K(Clqo) \cdot \frac{1}{2}H_2O$ to $Cu(Clqo)_2$, can be easily interpreted as being due to the different bonding site of the oximato group; in fact the N-coordination increases the double-bond character of the N–O bond.

Several studies have been reported in the literature on oximes and related complexes, and analogous trends in the C=N and N–O stretching frequencies as a diagnostic feature of linkage isomerism of the oximato group have been observed [9a, 12].

As far as the heteropolynuclear complexes 2a and 2b are concerned, their IR spectra show the following characteristic features. In the C=O region they are very similar to the spectrum of $Cu(nqo)_2$, indicating that the carbonyl group is not significantly affected by polynucleation. The C=N stretching frequency is higher than that of $Cu(nqo)_2$ but slightly lower than that of $La(nqo)_3$, indicating an intermediate amount of electron delocalization. Stretching vibrations assignable to N–O groups are present either at 1180 cm^{-1} or at 1090 cm^{-1}; therefore we must deduce that both types of oximato groups, O-bonded and N-bonded, are present. While it seems reasonable to believe that the lanthanide ion is coordinated to $Cu(nqo)_2$ molecules mainly through the oximic oxygen atom (Scheme 1), it is more difficult to interpret the N–O band at 1180 cm^{-1}. It could be due to the presence of a $Cu(nqo)_2$ unit only weakly bonded to Ln^{3+}; another reasonable hypothesis is that a copper(II) centre is chelated by nqoH molecules behaving as neutral ligands. In this case the protons could be shared between two or more atoms and thus might not appreciably affect the stretching frequency of N–O groups. In fact it has been reported in the literature that the IR spectrum of a copper(II) complex containing the protonated $ClqoH_2^+$ species does not differ from that of the parent compound $Cu(Clqo)_2$ [3]. Chloride ions and water molecules would complete the coordination around the metal ions.



Scheme 1.

The electronic spectra of **2a**, **2b** and $Cu(nqo)_2 \cdot H_2O$ have been compared both in solution and in the solid state. The spectrum of $Cu(nqo)_2 \cdot H_2O$ in methanol is characterized by an intense band at 398 nm, typical of the ligand [8b], and a d–d band at 490 nm, which are slightly shifted in the spectrum of the solid (λ_{max} 380 and 508 nm, respectively). The shift of the d–d band can be reasonably explained in terms of an expansion of the coordination sphere; in fact $Cu(nqo)_2 \cdot H_2O$ is reported to be presumably dimeric in solution (with a square-pyramidal coordination of the metal) and polymeric (and thus hexa-coordinated) in the solid state [3]. The solution spectra of **2a** and 2b are identical with that of $Cu(nqo)_2 \cdot H_2O$ under the same conditions; this indicates that **2a** and **2b** are unstable in solution, reverting to the parent compound $Cu(nqo)_2$. A significant difference appears instead in the spectra of solid **2a** and **2b**, which are characterized by one broad band at *ca.* 420 nm with a slight shoulder at 510 nm. This unique band probably results from superimposition of the unshifted d–d band of the Cu^{II} chromophore at 510 nm with the nqo band shifted to higher wavelengths. These data might indicate that the geometry of the copper(II) ion is not appreciably affected upon polynucleation onto Ln^{III}, while the nqo ligand finds itself in a different situation, perhaps bridging two different metal ions, as inferred from the IR spectrum too.

It is worth noting here that the reaction reported above, carried out with chlorides of heavier lanthanides (Sm, Gd, Tb, Er), produces polymeric products of ill-defined composition, having a much lower lanthanide content. Perhaps the smaller size of the above-mentioned cations, compared to La^{III} and Nd^{III}, can account for this behaviour.

Minor, although interesting, modifications are produced in the $Cu(nqo)_2 \cdot H_2O$ molecule on reaction with lanthanide perchlorates (Ln = La, Nd, Sm, Tb, Er). Whatever the lanthanide used, an identical dark red microcrystalline product is obtained, which can be tentatively formulated as $Cu_2(nqo)_3ClO_4 \cdot \frac{1}{2}(nqoH) \cdot 2H_2O$ (**3**), on the basis of the analytical and thermogravimetrical data. As for the compounds **2** described above, the homogeneity of the sample was verified by X-ray fluorescence spectroscopy.

A gradual weight loss occurred between 40 °C and 170 °C (found 13.5%; calc. for $\frac{1}{2}$(nqoH) and $2H_2O$, 14.1%); a successive violent endothermic decomposition between 208 °C and 214 °C (weight loss 85.5%) is attributable to the presence of a perchlorate group. This is also demonstrated by the IR spectrum which shows a broad intense band at 1070–1125 cm^{-1} and a weak one at 625 cm^{-1}, due respectively to the ν_3 and ν_4 vibrations of the uncoordinated perchlorate ion in T_d symmetry [13]. In the other regions, the spectrum of compound **3** is very similar to that of $Cu(nqo)_2 \cdot H_2O$, except for the presence of two distinct bands of comparable intensity in the C=N region (1520 and 1550 cm^{-1}), which indicate the presence of both chelated and non-chelated nqo ligands. While the N-bonded N–O group is clearly present (stretching vibration at 1180 cm^{-1}), the O-bonded N–O stretching cannot be identified with certainty due to interference with the ClO_4^- band.

The electronic spectra of compound **3** are surprisingly quite similar to those of compounds **2a** and **2b** described above, both in solution and in the solid state. This indicates that **3** is unstable in solution, returning to $Cu(nqo)_2$, and that the chromophores of compound **2** and **3** are strictly similar.

The reasons for the different reactivities of lanthanide chlorides and perchlorates toward *o*-quinone monooximato copper(II) complexes are not apparent; probably they can be found in the higher Lewis basicity of the chloride which might stabilize the heteropolynuclear complex. We may also recall that lanthanide ions show a marked tendency to form polymeric chains through double or triple chloride bridges [14]. This might suggest the hypothesis that polynucleation with $Cu(nqo)_2$ is stabilized by μ-chloro ligands.

A comparison of the magnetic data of the above-described complexes can give some information about the metal–metal interaction.

The homopolynuclear complex **3** has a magnetic moment of 1.62 BM, in agreement with an antiferromagnetic interaction between the metal centres.

In the copper–lanthanum complex, the magnetic moment (μ_{eff} = 3.88 BM) is due only to the presence of the copper(II) ions, the lanthanum ions being diamagnetic; a comparison of these data with that obtained for the copper–neodymium analogue (μ_{eff} = 6.29 BM) suggests that a magnetic interaction is operating also in this complex.

However, these observations need a deeper study owing to the complexity of the molecules and the lack of information on crystal structures.

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