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Note

Cu–O stretching frequency correlation with phenanthroline pK_a values in mixed copper complexes

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Abstract

A study of Cu–O vibration frequencies in 32 isostructural mixed copper complexes containing eight differently substituted phenanthrolines and four different oxygen donor bidentate ligands, is presented. In all cases linear correlation was found between phenanthroline pK_a values and the studied vibration frequencies, suggesting that an increase in phenanthroline basicity weakens Cu–O bonds in this type of compound. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

As part of an extensive study [1-8] dealing with copper ternary chelates of general types Cu(N-N)- $(O-O)^+$ and Cu(N-N)(O-O), where N-N is an aromatic diimine and O-O is acetylacetonate or salicylaldehydate in the first case, and oxalate or malonate in the second, we have studied the frequency variations in their Cu-O vibrations. In this paper, complexes with substituted 1,10-phenanthrolines are discussed. These phenanthrolines (X-phen) are: 1,10-phenanthroline (phen), 4,7-dimethyl-1,10-phenanthroline (4,7dmphen), 5,6-dimethyl-1,10-phenanthroline (5,6dmphen), 3,4,7,8tetramethyl-1,10-phenanthroline (3,4,7,8tmphen), 4,7diphenyl-1,10-phenanthroline (4,7d\phen), 5-methyl-1,10-phenanthroline (5mphen), 5-phenyl-1,10-phenanthroline (5\phiphen) and 5-nitro-1,10-phenanthroline (5NO₂phen).

This type of complex has been thoroughly studied in solution since the publication of several reports on the anomalous behaviour of the equilibrium [9,10]

 $Cu(N-N)^{2+}_{(aq)} + (O-O)^{n-}_{(aq)} \rightleftharpoons Cu(N-N)^{(2-n)+}_{(aq)}$

Contrary to what is expected on a statistical basis, the equilibrium constant for this reaction is found to be larger than for

$$\operatorname{Cu}_{(\operatorname{aq})}^{2+} + (O-O)_{(\operatorname{aq})}^{n-} \rightleftharpoons \operatorname{Cu}(O-O)_{(\operatorname{aq})}^{(2-n)+}$$

whenever N–N is a good π -acceptor ligand.

Sigel et al. [9,10] explained this behaviour based on the HSAB principle [11,12]. A π -acceptor ligand bound to a copper ion will withdraw electron density, making $[Cu(N-N)]^{2+}$ a harder acid, which will consequently be preferred, as opposed to the simple aqueous Cu²⁺ ion, by hard bases such as oxygen donors.

Different substituents on a phenanthroline molecule affect its basicity, or σ -donor ability, in a way easily measured by pK_a values (Table 1). However, the effect of these same substituents on the π -acceptor properties of phenanthroline is not easily evaluated, even though it is expected to be of significant importance and to affect bonding parameters in the molecule. An experimental parameter widely accepted to indirectly measure these properties is the half wave potential for the N-N/ N-N⁻ pair. Sanna et al. [13] have obtained $E_{1/2}$ values for seven of the eight phenanthrolines studied in this paper, which have an inverse correlation with pK_a values. Solution equilibrium studies to determine the

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Phenanthrolines	pK _a ^a
3,4,7,8-Tetramethyl-1,10-phenanthroline	6.31
4,7-Dimethyl-1,10-phenanthroline	5.95
5,6-Dimethyl-1,10-phenanthroline	5.60
5-Methyl-1,10-phenanthroline	5.27
1,10-Phenanthroline	4.93
5-Phenyl-1,10-phenanthroline	4.90
4,7-Diphenyl-1,10-phenanthroline	4.80
5-Nitro-1,10-phenanthroline	3.22

^a All values were taken from Ref. [21], except for 3,4,7,8-tetramethyl-1,10-phenantroline, which was taken form Ref. [22].

formation constants of metal complexes with substituted phenanthrolines are not feasible because of their increased hydrophobic character which makes them and their metal complexes quite insoluble. Thus, in order to study the differences in strength interaction of copper(II) with oxygen donors, the variations on the Cu-O stretching frequencies have been analysed in this work.

The results obtained in this work are consistent with similar studies concerning Quantitative Analysis of Ligand Effects (QALE, [14–16]) in which it has been suggested that the π -acceptor properties of a ligand decrease regularly as their σ basicity increases [17]. However, most of these studies became important in organometallic chemistry, where the dual π -acceptor/ σ donor character of ligands such as phosphines is claimed to be responsible for measurable changes in various physicochemical properties of their complexes. However, until now, this type of analysis has never dealt with either copper or phenanthroline complexes.

All complexes studied here are five-coordinated with a distorted square pyramidal geometry, with an oxygen atom either from a water molecule or a nitrate ion on the apical position [1-7,18-20].

2. Experimental

2.1. Materials

All eight differently substituted 1,10-phenanthrolines (X-phen), acetylacetone, salicylaldehyde, potassium oxalate, malonic acid and $Cu(NO_3)_2 \cdot 2.5H_2O$ were reagent grade, obtained from Aldrich Chemical.

2.2. Analyses and spectroscopical measurements

Complexes were characterised by standard techniques. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

2.2.1. IR spectra

All measurements were carried out in a Nicolet 740 FT-IR spectrophotometer. Mid-IR spectra were obtained in KBr pellets from 4000 to 400 cm⁻¹ and in polyethylene pellets in the 700–70 cm⁻¹ region. Resolution was better than 1 cm⁻¹.

2.3. Synthesis of the complexes

2.3.1. [Cu(X-phen)(salal)]NO₃ and [Cu(X-phen)(acac)] NO₃

Phenanthroline (0.5 mmol) was dissolved in 10 ml of a 1:4 ethanol-water mixture and was then added to 0.5 mmol of Cu(NO₃)₂ · 2.5H₂O previously dissolved in 5 ml of water. To this mixture, 5 ml of a 0.1 M solution of the O-OH ligand were added, followed by dropwise neutralisation with a 10% aqueous ammonia solution. Dark green crystals were collected 1 day after for the salicylaldehydate complexes and dark blue needles were obtained for the acetylacetonate complexes.

2.3.2. [Cu(X-phen)(ox)]

Copper oxalate was prepared by mixing equimolar quantities of $Cu(NO_3) \cdot 2.5H_2O$ and potassium oxalate in water. The $[Cu(ox)]_n$ precipitate was filtered and air dried; 0.5 mmol were suspended in water and 0.5 mmol of the corresponding diimine dissolved in ethanol was added with stirring. The precipitate dissolved to form a deep blue solution, which was left to crystalise.

2.3.3. [Cu(X-phen)(mal)]

A total of 0.5 mmol of the corresponding diimine dissolved in methanol were added to 5 ml of a 0.1 M solution of $Cu(NO_3)_2 \cdot 2.5H_2O$. To this solution, 5 ml of a 0.1 M malonic acid solution were added, followed by neutralisation with 10% aqueous ammonia solution. This formed a deep blue solution from which crystals were collected.

3. Results and discussion

Characterisation data obtained for all the complexes studied, which included X-ray structure determination for several complexes, supported the assumption that they all have the same structure as regards to the coordination environment around the copper atom. Assignment of Cu–O bands was thus easily achieved, and variations in these frequency values for each family of complexes may be solely attributed to variations in bond strength. These frequencies are shown in Table 2.

Table 2

Analysed Cu-O vibration frequencies (cm⁻¹) in mixed copper complexes^a

Complex	$v_1 ({\rm cm}^{-1})$	$v_2 ({\rm cm}^{-1})$	Complex	$v_1 ({\rm cm}^{-1})$	$v_2 ({\rm cm}^{-1})$
$L^1 = acac^-$			$L^3 = ox^{2-}$		
¹⁸ [Cu(phen)(acac)]NO ₃	592	275	20 [Cu(phen)(ox)]	546	_
[Cu(4,7dmphen)(acac)]NO ₃	_	266	[Cu(4,7dmphen)(ox)]	529	413
[Cu(5,6dmphen)(acac)]NO ₃	590	267	[Cu(5,6dmphen)(ox)]	527	410
$[Cu(3,4,7,8tmphen)(acac)]NO_3$	587	262	[Cu(3,4,7,8tmphen)(ox)]	528	412
[Cu(4,7d\phen)(acac)]NO ₃	593	273	[Cu(4,7d\phen)(ox)]	_	427
[Cu(5mphen)(acac)]NO ₃	592	266	[Cu(5mphen)(ox)]	542	417
[Cu(5\phen)(acac)]NO ₃	593	270	[Cu(5\phen)(ox)]	550	425
[Cu(5NO ₂ phen)(acac)]NO ₃	_	283	[Cu(5NO ₂ phen)(ox)]	570	436
$L^2 = salal^-$			$L^4 = mal^{2-}$		
¹ [Cu(phen)(salal)]NO ₃	546	528	¹⁹ [Cu(phen)(mal)]	366	331
³ [Cu(4,7dmphen)(salal)]NO ₃	534	509	[Cu(4,7dmphen)(mal)]	359	320
⁶ [Cu(5,6dmphen)(salal)]NO ₃	536	513	² [Cu(5,6dmphen)(mal)]	360	325
⁴ [Cu(3,4,7,8tmphen)(salal)]NO ₃	531	498	[Cu(3,4,7,8tmphen)(mal)]	357	318
⁵ [Cu(4,7d\phen)(salal)]NO ₃	547	532	⁷ [Cu(4,7d\phen)(mal)]	359	320
[Cu(5mphen)(salal)]NO ₃	_	530	[Cu(5mphen)(mal)]	360	325
[Cu(5\phen)(salal)]NO ₃	_	535	[Cu(5\phen)(mal)]	366	331
[Cu(5NO ₂ phen)(salal)]NO ₃	547	533	⁷ [Cu(5NO ₂ phen)(mal)]	363	347

^a [1-7] and [18-20] are the references for crystal structure of the compounds.



Fig. 1. Cu–O vibrations vs. phenanthroline p K_a in [Cu(X-phen)(acac)]NO₃. \blacksquare , ν (Cu–O), correlation coefficient r = -0.98079; \blacktriangle , δ (O–Cu–O), correlation coefficient r = -0.95382.

3.1. $[Cu(X-phen)(acac)]NO_3$

Assignment of Cu–O related vibrations in these mixed complexes was based on Mikami's [23] normal coordinate analysis for Cu(acac)₂. All mixed complexes exhibit a band slightly below 600 cm⁻¹ assigned to v(Cu–O), and another between 262 and 283 cm⁻¹ assigned to δ (O–Cu–O). These two bands could be identified in all spectra for the mixed complexes in this family, and their corresponding frequencies are shown in Table 2.

It can be seen from Fig. 1 that both of these Cu–O related frequencies decrease linearly as the substituted phenanthrolines σ -donor strength (p K_a) increases.

3.2. [Cu(X-phen)(salal)]NO₃

Salicylaldehydate complexes' IR spectra were studied by Percy and Thornton [24], who assigned two bands at 552 and 539 cm⁻¹ as v(Cu-O). The salicylaldehydate mixed complexes in this work display these two bands, which are listed in Table 2. It can

be seen from Fig. 2, that both frequencies have a very good linear correlation with the substituted phenan-throline pK_a values.

3.3. [Cu(X-phen)(ox)]

Oxalate can easily act as a bridging ligand between two metal atoms, and several binuclear complexes with copper and nitrogen donor chelates have been reported [25,26]. To ensure the formation of mononuclear complexes exclusively, the synthetic procedure for this family of complexes excludes anionic species, needed to stabilise binuclear complexes of the type (N-N)Cu-oxalato- $Cu(N-N)^{2+}$. Analysis of copper-oxygen vibrations in these complexes was based on Fujita's study on $K_2[Cu(ox)_2]$ [27]. In spite of the fact that, in this complex, copper-oxygen vibrations are coupled with other vibrations that do not compromise the Cu-O bond, their frequencies (Table 2) correlate with substituted phenanthroline pK_a values quite satisfactorily (Fig. 3).



Fig. 2. Cu–O vibrations vs. phenanthroline pK_a in [Cu(X-phen)(salal)]NO₃. \blacksquare , ν (Cu–O)₁, correlation coefficient r = -0.98793; \blacktriangle , ν (Cu–O)₂, correlation coefficient r = -0.96584.



Fig. 3. Cu–O vibrations vs. phenanthroline pK_a in [Cu(X-phen)(ox)]. \blacksquare , v[(Cu–O) + (C–C)], correlation coefficient r = -0.96767; \blacktriangle , v[(Cu–O) + ring def.], correlation coefficient r = -0.93171.



Fig. 4. Cu–O vibrations vs. phenanthroline pK_a in [Cu(X-phen)(mal)]. \blacksquare , v(Cu–O)₁, correlation coefficient r = -0.93236; \blacktriangle , v(Cu–O)₂, correlation coefficient r = -0.981.

3.4. [Cu(X-phen)(mal)]

For this family of complexes, assignment of copperoxygen vibrations could not rely on previous work done on related binary copper malonate complexes, as no such information could be found. Assignment was achieved, however, by analysing the spectra of five complexes with the formula $K_2[M(mal)_2]$ for M = Mn, Co, Ni, Cu and Zn, prepared for this purpose. All these complexes display one band in the 320-360 cm⁻¹ range, not present in the free malonic acid spectrum. An excellent correlation was found between the frequency of this band and the stability constants of the complexes [28], suggesting a significant Cu-O character for this absorption [29]. All mixed complexes of the type [Cu(X-phen)(mal)], exhibit two bands in this interval. The corresponding frequencies are listed in Table 2, and both show a good correlation with the substituted phenanthroline pK_a values (Fig. 4).

Based on our observations, we can state that, for complexes of the type $[Cu(N-N)(O-O)]^+$ or [Cu(N-N)-(O-O)], where N–N are substituted phenanthrolines, an increase on the σ basicity of the N–N ligand produces a weakening of the Cu–O bond, based on the variations in their corresponding IR frequencies. This, together with reported $E_{1/2}$ values for these phenanthrolines, which are more negative as their p K_a increases, is in agreement with Drago's suggestion that π -acidity of a ligand increases as its σ basicity decreases. All these considerations are consistent with Sigel's hypothesis that the enhancement in Cu–O interaction is caused by the π acceptor properties of the N–N ligand. This, of course, does not rule out the consideration that σ and π effects can act synergetically.

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