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Electronic and X-Ray Photoelectron Spectra of Copper Catecholate Complexes

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The electronic and X-ray photoelectron spectra (XPS) of a number of copper(II) catecholato complexes are reported. The electronic spectra exhibit a rather intense visible absorption. Comparison of trends in the position of this intense absorption with the copper 2p binding energies supports the view that the visible 3h absorption is due to a copper → catecholato (π) transition.*

Introduction

We have been interested for some time in catecholate complexes of transition metals because we view these as models for the enzyme–substrate complex of the aromatic dioxygenases [1–6]. In particular, we have prepared a variety of ternary complexes containing one catecholato type ligand bound to a metal [1–3, 5]. Of these, the copper(II) systems have proven most interesting because of the fact that in the presence of oxygen the catecholato ligand appears to undergo intradiol ring cleavage [3, 5]. This ring opening reaction is formally similar to that carried out by a number of intradiol dioxygenases [6]. The ternary copper complexes which we have prepared have another interesting property which we will address in this paper. This is the fact that in the visible region of the electronic spectrum a rather strong absorption is frequently observed. In several cases the extinction coefficient for this prominent absorption is well over 10^3 l mol^{-1} cm^{-1}, a rather unusual feature.

Amundsen, *et al.*, have assigned a spectral band found in the visible region of a copper–phenolate system to a copper → phenolate O(π*) transition [7]. It appeared to us that the rather intense visible band observed in our copper catecholato systems could also be due to a copper → catecholato O(π*) transition. As a test of this assignment we have attempted to correlate the position of the prominent visible absorption band with the copper binding energies as determined by X-ray photoelectron spectroscopy (XPS). In this paper, we report both the electronic spectral and XPS properties of several ternary copper catecholate complexes which contain one catecholate ligand and one bidentate nitrogen donor ligand. Comparison of the information obtained from both techniques indicates that the prominent visible absorption is, indeed, due to a copper → catecholato O(π*) transition.

Experimental

The copper catecholato complexes were prepared as previously described [2, 5]. In the text and tables, abbreviations are used when discussing the compounds. These abbreviations are explained as follows: cat = pyrocatechol dianion; DBcat = 3,5-di-t-butylcatechol dianion; 3Ncat = 3-n-nonylcatechol dianion; en = ethylenediamine; tmen = N,N,N′,N′-tetramethylethylenediamine; phen = 1,10-phenanthroline; bipy = 2,2′-bipyridyl.

Electronic spectra were recorded with a Beckman Acta MVII spectrometer. In most cases, solution spectral data are reported. A few of the compounds were insoluble in solvents of interest and in these cases reflectance data are given. XPS spectra were recorded on a Varian V-IEE 15 high-resolution electron spectrometer equipped with a 620-L on-line computer (8 K). During the course of the measurement, the sample was maintained at approximately 100 K by cooling with liquid nitrogen. This has normally proven satisfactory to minimize decomposition reactions caused by the X-ray beam [8–10]. Some of the compounds were observed to decompose to copper(I) when spectra were recorded at room temperature. This photoreduction was completely prevented at the lower temperature. The samples were run as finely ground powders dusted onto the backing of a one-sided adhesive cellotape which was attached to the cylindrical sample holder. The spectra were standardized with the C-1s aliphatic hydrocarbon line for which a binding energy of 284.0 eV was assigned [11]. All spectra were time averaged and smoothed using a box car function.

Results

Figures 1 and 2 show the electronic spectra of two series of the compounds studied. Figure 1 demonstrates spectra for complexes of 3,5-di-t-butylcatechol while Fig. 2 shows spectra for 3-n-nonylcatechol complexes. In the UV region, spectra for a few of the compounds are not given because of the fact that the spectral features in this region are rather similar and do not appear to arise from transitions involving the catecholato ligand. Table I summarizes all the electronic spectral data.

The XPS spectra obtained were all completely typical for copper(II) [8–10]. The copper $2P_{3/2}$ spectral data are summarized in Table II. The spectra all demonstrated a main peak with a binding energy in the neighborhood of 934 eV with a somewhat asymmetrical shake-up satellite at about 9 eV to the high

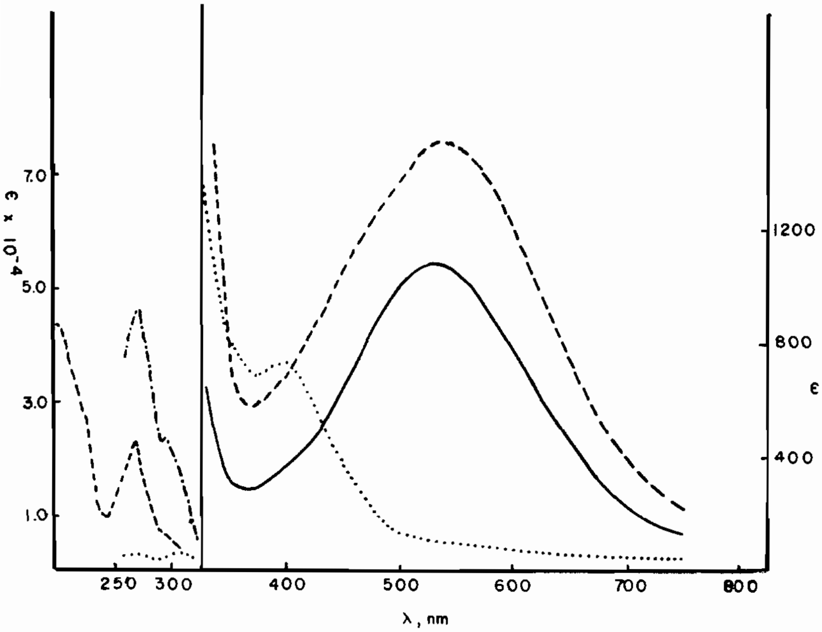

Fig. 1. Electronic spectra for Cu(phen)(DBcat)(– – – –), Cu(bipy)(DBcat)(——), Cu(en)(DBcat)(••••••), Cu(phen)Cl_2 (•—•—•—) u.v. region only.

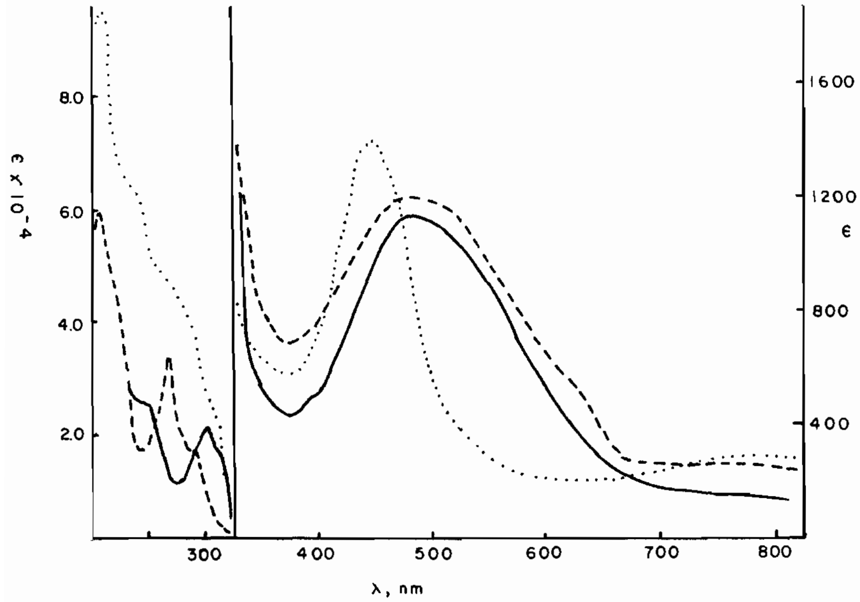

Fig. 2. Electronic spectra for Cu(phen)(3Ncat)(– – – –), Cu(bipy)(3Ncat)(——), Cu(en)(3Ncat)(•••••).

TABLE I. Visible Spectra for Copper(II) Catecholates.

Compound	λ max (ε)
Cu(bipy)(cat)	480[a]
Cu(phen)(cat)	490[a]
Cu(en)(cat)	440[a]
Cu(tmen)(cat)	415 (540)
Cu(bipy)(DBcat)	530 (2000)
Cu(phen)(DBcat)	535 (1000)
Cu(en)(DBcat)	395 (740)
Cu(tmen)(DBcat)	410 (920)
Cu(bipy)(3Ncat)	492 (1140)
Cu(phen)(3Ncat)	498 (1220)
Cu(en)(3Ncat)	440 (1420)
Cu(tmen)(3Ncat)	448 (1230)
Cu(phen)Cl_2	695 (33)

[a] Reflectance data.

TABLE II. Copper $2P_{3/2}$ XPS Parameters for Copper(II) Catecholates.

Compound	Binding Energy, eV	
	Main peak	Satellite
Cu(bipy)(cat)	933.3	942.3
Cu(phen)(cat)	933.2	942.3
Cu(en)(cat)	934.2	943.8
Cu(bipy)(DBcat)	933.5	942.4
Cu(phen)(DBcat)	933.6	942.3
Cu(en)(DBcat)	934.2	943.8
Cu(tmen)(DBcat)	933.9	943.0
Cu(bipy)(3Ncat)	933.9	942.2
Cu(phen)(3Ncat)	933.6	941.8
Cu(en)(3Ncat)	934.2	942.6

binding energy side of the main peak. The satellite peak was somewhat asymmetrical with two unresolved components. The satellite intensity was consistently about 30% the total intensity for the $2P_{3/2}$ region. These characteristics are quite normal for copper(II) in a 2N, 2O ligand environment. The $2P_{1/2}$ region revealed similar information.

Discussion

XPS Spectra

All of the copper $2P_{3/2}$ XPS data are summarized in Table II. The XPS properties are quite normal for copper(II) complexes. As is always the case for copper(II) with nitrogen or oxygen donors, a shake-up satellite is observed at higher binding energy from the main peak. The satellite peak which is usually composed of two components is a somewhat asymmetrical peak. The splitting between the main peak and the satellite peak varies from about 8 to 9.5 eV, also quite normal for copper(II) with 2 nitrogen and 2 oxygen donor atoms. The corresponding binding energy parameters for the copper $2P_{1/2}$ peaks parallel those reported for the $2P_{3/2}$ peaks and, therefore, are not separately reported here. The values for the ligand nitrogen 1S binding energies have also been determined. Little variation in these values is observed throughout the series of compounds. In general, it is observed that the N 1S binding energies for the ethylenediamine ligands are slightly higher than those for the diimine ligands.

Electronic Spectra

Figures 1 and 2 and Table I give the pertinent electronic spectral parameters. Although the primary interest here will be the intense visible band, attention will first be given to the ultraviolet region of the spectra. Normally in the region between 350 nm and 220 nm, two principal absorptions are observed, sometimes with additional shoulders present. It appears that they are due primarily to the bidentate nitrogen ligand. For example, the spectra of Cu(phen)(DBcat) and Cu(phen)Cl_2 are quite similar in the u.v. region. In this spectral region, we expect to find an $N(\sigma) \rightarrow Cu_{d_{x^2-y^2}}$ charge transfer transition as well as the intra-ligand transition for phenanthroline. Note that the u.v. spectrum of Cu(phen)Cl_2 is included in Fig. 1 for comparison. The catechol intraligand transitions which also occur in this region of the spectrum are apparently not observed as separately resolved peaks. Thus, in general, in the u.v. region we observe spectral features due primarily to the nitrogen counter ligand bound to the copper center.

The visible spectra of the complexes show one absorption which is, in most cases, rather intense ($\epsilon > 10^3$ l mol^{-1} cm^{-1}). This band cannot be due to a copper d–d transition. The intensity is far too great for a d–d transition and the position of the band (*ca.* 440–535 nm) occurs at too high energy for a d–d transition. Normally, one would expect to find the d–d band in the region 600–750 nm with an intensity on the order of 10^2 l mol^{-1} cm^{-1} or less. The strong visible band in many of the complexes is somewhat asymmetrical and seems to contain a low intensity component on the long wavelength side which is probably due to a weak d–d absorption. A well-resolved d–d band is not observed for any of the complexes. The strong visible band is clearly due to the presence of the catecholate ligand for it is completely absent in complexes not containing the catecholato species, *i.e.* Cu(phen)Cl_2. Possible assignments for this band could be $O(\sigma) \rightarrow Cu_{d_{x^2-y^2}}$ or copper → catecholate π^* transitions. As pointed out by Amundsen, *et al.*, the position of an $O(\sigma) \rightarrow Cu_{d_{x^2-y^2}}$ transition would be expected to occur in the region of 250 nm (40,000 cm^{-1}) [7]. Therefore, this band, which is observed in the region of 500 nm (20,000 cm^{-1}) could not be reasonably assigned to a O(σ) → $Cu_{d_{x^2-y^2}}$ transition. If the band were due to a copper → catecholate π^* transition, it should be possible qualitatively to correlate the copper binding energy, as measured by XPS, with the position of the visible band. Thus, for an electronic transition originating on copper, one should observed for those complexes with the lowest binding energy a lower energy, longer wavelength, visible absorption. While it is certainly true that one must be careful not to draw too many conclusions from relatively small changes in core electron binding energies, it was anticipated that the qualitative trends should correlate roughly with the position of the visible charge transfer absorption.

If one inspects the position of the visible band within a series of compounds containing the same catecholato ligand with the various nitrogen counter ligands (Table I), one invariably observes that the complexes with the simple saturated nitrogen ligands, en or tmen, show the visible transition consistently at higher energy (2000–3000 cm^{-1}) than do the complexes with unsaturated diimine ligands. In the XPS spectra one observes that the complexes with en or tmen nitrogen ligands show the main Cu $2P_{3/2}$ peak at higher binding energy than those with a diimine ligand. Thus, the anticipated qualitative correlation between binding energy and the position of the visible band is indeed observed. A lower energy electronic transition is observed in the compounds with a relatively lower binding energy. The compounds with a lower binding will have slightly higher d orbital energies. If one assumes a relatively constant energy for the catecholato π^* orbitals, a copper → catecholato π^* transition should then occur at lower energy as observed. Therefore, it appears that the position of the Cu $2P_{3/2}$ main peak in the XPS spectrum is consistent with a copper → catecholato π^* assignment for this transition. This data is completely inconsistent with any ligand → copper charge transfer for the visible band. Therefore, from the information reported here, we would agree with the view of Amundsen, *et al.* [7] that a copper → ligand transition occurs in the visible region for copper–phenolate complexes. These authors have observed a second absorption at somewhat higher energy which they also assign to a copper → phenolate π^* transition. In the copper catecholate complexes, we do not observe such a second transition although it is possible that the single (sometimes asymmetrical) visible band involves transitions to more than one catecholato π^* orbital.

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