Synthesis and Spectroscopic Investigation of Mixed-Ligand Copper Chelates containing 2-Hydroxyaryloximes and N-disubstituted Dithiocarbamates. Crystal and Molecular Structure of Trans-bis[propanone, 1-(2-hydroxy-phenyl)oximato] Copper(II)

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Abstract. A series of mixed-ligand copper(II) chelates containing the anion of 2-hydroxyaryloxime(oxime) and N,N-disubstituted dithiocarbamate(dtc), [Cu(dtc)(oxime)], was prepared and characterised. The spectra (IR, ESR, electronic excitation) indicate that the CuNOS₂ chromophore attains square planar geometry. The ESR observables suggest appreciable covalency. In the case of [Cu(Et₂dtc)(oxime)] chelates, however, the observed data suggest distortion from square planar arrangement to a square pyramidal, indicative of a possible dimerism.

In addition, the structure of the trans-bis[propanone, 1-

(2-hydroxyphenyl)-oximato]copper(II), Cu(C₉H₁₀NO₂)₂ was determined by X-ray diffraction (monoclinic, space group P2₁/n, a = 12.072(7) Å, b = 5.204(2) Å, c = 13.571(6) Å, $\beta = 103.72(1)^{\circ}$, Z = 2). The molecule consists of discrete Cu(ppox)₂ monomeric units, where the Cu atom is in the equatorial plane bonded to two nitrogen atoms and two oxygen at distances of 1.949(2) and 1.882(2) Å, respectively.

Keywords: Mixed-ligand Cu^{II} chelates; 2-OH aryloximes; Dithiocarbamates; Spectra; Crystal structure; [Cu(ppox)₂]

Synthese und spektroskopische Untersuchung von gemischten Kupfer-Chelaten von 2-Hydroxyaryloxim und N-substituierten Dithiocarbamaten. Kristall- und Molekularstruktur von trans-Bis[propanon, 1-(2-hydroxyphenyl)-oximato]Kupfer(II)

Inhaltsübersicht. Kupfer(II) Chelate mit den Anionen von 2-Hydroxyaryloxim (oxime) und N,N-disubstituieren Dithiocarbamaten (dtc), [Cu(dtc)(oxime)], wurden dargestellt und charakterisiert. Die Spektren (IR, ESR, elektronische Anregung) zeigen, daß die chromophore Einheit CuNOS₂ quadratisch planar ist. ESR-Beobachtungen indizieren einen starken covalenten Charakter. Bei den Chelaten [Cu(Et₂dtc)(oxime)], deuten die experimentellen Daten auf eine Verzerrung zu einer quadratischen Pyramide, was möglicherweise auf eine Dimerisierung hinweist. Die Struktur des trans-bis[propanon,1-(2-hydroxyphenyl)oximato]Kupfer(II), Cu(C₉H₁₀NO₂)₂, wurde röntgenographisch bestimmt (monoklin, Raumgruppe P2₁/n, a = 12.072(7) Å, b = 5.204(2) Å, c = 13.571(6) Å, β = 103.72(1)°, Z = 2). Das Molekül besteht aus isolierten monomeren Cu(ppox)₂-Einheiten, in denen das Cu Atom in der äquatorialen Ebene liegt und an zwei Stickstoff- und zwei Sauerstoffatomen in Abständen von 1.949(2) bzw. 1.882(2) gebunden ist.

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Introduction

Although there is an extensive literature on binary metal complexes of 2-OH aryloximes [1-3] and on those of dithiocarbamates [4], there are only a few reports on mixed-ligand complexes of the above ligands [5, 6]. In this respect, were prepared and characterized a series of 18 mixed-ligand copper(II) chelates corresponding to the general formula [Cu(dtc)(oxime)], where **dtc** is the anion of the dithiocarbamate ligand

(I) and **oxime** is the anion of the 2-OH aryloxime ligand (II).



Scheme 1 Schematic representation of dithiocarbamate(I) and oximate(II) anion

Their IR, ESR and electronic excitation spectra were measured and analyzed in order to examine the coordination behaviour and the covalency of metal-ligand bond of the chelates. The compounds prepared, their elemental analyses and some physicochemical data are listed in Table 1.

In addition, the crystal and molecular structure of the trans-bis[propanone,1-(2-hydroxyphenyl)-oximato]copper(II), abbreviated as bis(2-OHpropiophenoneoximato)copper(II), [Cu(ppox)₂], was investigated as part of a research program on copper(II) 2-OH oximates developed in our laboratory [2, 7] with the object of gaining information on Cu–O and Cu–N bonds and on the structures of oxime ligands.

Experimental

Preparation of the complexes. The hydrated copper(II) chloride and the sodium hydroxide were purchased from Fluka. The synthesis of sodium dithiocarbamates, $NaR_2dtc \cdot 2H_2O$, {N,N-diethyldithiocarbamate (Et₂dtc), N,N-dibenzyldithiocarbamate (Benz₂dtc) and piperidinodithiocarbamate (Pipdtc)} and of 2-hydroxyaryloxime ligands {salicylaldoxime (Hsaox), 2-OHacetophenoneoxime (Hapox), 2-OHpropiophenoneoxime (Hppox), 5-CH₃, 2-OHacetophenoneoxime (Hmpox), 2-OHbenzophenone-oxime (Hbpox) and 4-OCH₃, 2-OHbenzophenoneoxime (Hopox)} was achieved employing literature methods [8, 9]. The mixed-ligand copper(II) complexes were prepared by the following way:

An aqueous solution (20 ml) of $CuCl_2 \cdot 2H_2O$ (4 mmol) was added dropwise to a mixture of equimolar quantities of sodium dithiocarbamate, 2-hydroxyaryloxime and sodium hydroxide in 50 ml of mixed solvent acetone-methanol-water (2:1:1). The solution mixture was stirring for 3 hours at 20 °C and the complex separated out as light brown solid. It was filtered off, washed with H₂O and MeOH and dried in vacuum (yield 85–95%). The copper(II) complexes are stable in the air, both in the solid state and in solution and are soluble in CH₂Cl₂, CH₃CN, DMF and DMSO but insoluble in MeOH, CH₃COCH₃ and H₂O. Although the solubility of the prepared complexes offers the possibility of obtaining crystalline samples for X-ray studies, there was no success after numerous attempts made on this purpose.

Preparation of trans-bis[propanone, 1-(2-hydroxyphenyl)-oximato]Copper(II), [Cu(ppox)₂]. The synthesis of Cu(ppox)₂ was achieved by reacting 10 mmol of the oxime Hppox and 5 mmol of an aqueous solution of CuCl₂, slightly acidified with hydrochloric acid [2]. The resulting solid filtered, washed with EtOH and dried in vacuo. The crude product was recrystallized from methylenechloride-ether solution. In the final stage, refrigeration allowed slow formation of olivegreen crystalls (m. p. 226-228 °C) suitable for X-ray diffraction studies.

Physical measurements and determinations. Stoichiometric analyses (C,H,N) were performed on a Perkin-Elmer 240 B

Table 1 Elemental analyses and physicochemical data of the mixed-ligand copper(II) complexes, [Cu(dtc)(oxime)]

	Complex	M. P. °C	C %	N %	H %	Cu %	$\mu_{ m eff}$ BM
1 2	[Cu(Pipdtc)(saox)]	202–204	43.92(43.38) ^a)	7.25(7.78)	4.94(4.48)	17.31(17.64)	1.78
	[Cu(Pipdtc)(apox)]	220–222	44.98(44.22)	7.29(7.59)	4.82(4.92)	16.27(16.98)	1.88
- 3 4	[Cu(Pipdtc)(mpox)] [Cu(Pipdtc)(ppox)]	212–214 201–203	45.91(46.43) 46.61(47.02)	7.25(7.22) 7.31(7.31)	5.05(5.19) 5.20(5.26)	15.93(16.37) 16.42(16.37)	1.89 1.83
5	[Cu(Pipdtc)(bpox)]	210–212	52.03(52.34)	6.33(6.42)	4.52(4.62)	14.19(14.57)	1.89
6	[Cu(Pipdtc)(opox)]	205–207	51.71(51.54)	6.18(6.01)	4.74(4.76)	13.38(13.63)	1.84
7	$[Cu(Et_2dtc)(saox)]$	174–176	41.04(41.42)	7.99(8.05)	4.73(4.64)	17.88(18.25)	1.73
8	[Cu(Et_2dtc)(apox)]	175–177	43.05(43.14)	7.57(7.74)	4.98(5.01)	17.23(17.55)	1.64
9	$[Cu(Et_2dtc)(mpox)]$	190–192	45.94(44.72)	7.07(7.45)	5.45(5.36)	16.76(16.89)	1.74
10	[Cu(Et_2dtc)(ppox)]	174–176	44.22(44.72)	7.22(7.45)	5.38(5.36)	16.53(16.89)	1.65
11	$[Cu(Et_2dtc)(bpox)]$	188–190	50.65(50.99)	6.23(6.60)	4.56(4.75)	14.48(14.98)	1.71
12	[Cu(Et_2dtc)(opox)]	173–175	49.73(50.98)	6.48(6.61)	4.65(4.75)	13.67(13.98)	1.74
13	[Cu(Benz ₂ dtc)(saox)]	181–183	56.73(55.98)	5.28(5.93)	4.38(4.27)	13.09(13.45)	1.83
14	[Cu(Benz ₂ dtc)(apox)]	173–175	56.41(56.83)	5.85(5.76)	4.63(4.56)	12.94(13.07)	1.74
15	[Cu(Benz ₂ dtc)(mpox)]	180–182	57.16(57.64)	5.73(5.60)	4.78(4.84)	12.61(12.70)	1.89
16	[Cu(Benz ₂ dtc)(ppox)]	171–173	56.94(57.64)	5.46(5.60)	4.73(4.84)	12.42(12.70)	1.75
17	[Cu(Benz ₂ dtc)(bpox)]	182–183	60.49(61.35)	5.63(5.11)	4.21(4.41)	11.39(11.58)	1.81
18	[Cu(Benz ₂ dtc)(opox)]	179–181	59.62(60.24)	4.25(4.85)	4.48(4.53)	10.77(10.98)	1.84

^a) Calculated values in parentheses.

elemental analyzer. The copper content was determined by the atomic absorption method on a Perkin-Elmer Mod. HGA 700 spectrometer 2100. Melting points were determined on a Reichert heated plate apparatus and are uncorrected. Molar conductivities were measured in acetonitrile solutions employing a WTW conductivity bridge and a calibrated dip type cell. Magnetic susceptibility measurements on powdered samples were performed at 25 °C employing the Faraday method on a home-built balance calibrated against Hg[Co(SCN)₄]. Diamagnetic corrections were estimated from Pascal's constants. Infrared spectra were recorded in the region 4000–200 cm⁻¹ on a FT-IR Perkin-Elmer 1600 spectrometer with samples in KBr discs.

Electronic absorption spectra in CH_2Cl_2 solutions and in Nujol mulls were obtained on a Shimadzu 160 A UV-Vis spectrometer. The ESR measurements were carried out on a standard X-band spectrometer type Bruker ESR-200 with magnetic field modulation 100 kHz. The measurements were performed at 20 °C on powdered samples and in frozen CH_2Cl_2 solutions at liquid nitrogen temperature.

X-ray crystallographic analysis. The crystal studied was a rectangular prism with dimensions $0.28 \times 0.20 \times 0.12$ mm and proved to be perfectly stable in the X-ray beam over the period of data aquisition. The X-ray beam was graphite monochromated MoK α radiation. The data were collected by means of a four-circle Phillips PW 1100-STOE PC automatically controlled X-ray diffractometer, on which the crystal of $Cu(ppox)_2$ was mounted. Systematic absences led to space group P2₁/n. Intensities of X-ray reflections were collected in the range $2 < \theta < 26^{\circ}$ with hkl: h = -3 to 14, k = -3 to 6, and l = -16 to 16. Three standard reflections were monitored periodically to detect systematic intensity changes during the course of the data collection. 3415 reflections were collected, from which 1603 unique were employed in the analysis. Due to the low absorption coefficient value ($\mu = 1.343 \text{ mm}^{-1}$) no correction for absorption was applied.

The copper(II) position was deduced from a three-dimensional Patterson synthesis and used to compute a firstapproximation electron-density synthesis, which revealed the position of all remaining non-hydrogen atoms. The hydrogen atoms were positioned geometrically. Refinement was carried out by full-matrix least-squares. The calculations were performed using the SHELX-86 and the SHELX-93 programs [10, 11]. The function minimised was $\Sigma w(|Fo^2| - |Fc^2|)^2$. $w = 1/[\sigma^2(Fo^2) + (0.045 P)^2 + 0.136 P]$ where and P = $[Max(Fo^2,0) + 2Fc^2]/3$. The final residual density max/min were $(\Delta(\rho))$ max/ $(\Delta(\rho))$ min) = 0.385/-0.223 e.Å⁻³ and the final values of agreement factors $R_1 = \Sigma(|Fo| - |Fc|)/\Sigma|Fo|$ and $wR_2 = [\Sigma w(|Fo^2| - |Fc^2|)^2/\Sigma w(|Fo|^4)]^{1/2}$ were 0.0311 and 0.0769 respectively. The figure of the thermal ellipsoids of the molecule and the clinographic projection of the unit cell were produced with the program ATOMS [12]. Structure factor tables and further crystallographic experimental details are available on request.

Results and Discussion

The reaction of the copper(II) ion with equimolar quantities of 2-hydroxyaryloxime and sodium dithiocarbamate resulted in the formation of brown solid almost quantitatively. The stoichiometric analysis of the isolated compounds (Table 1) are consistent with the general formula [Cu(dtc)(oxime)], while the molar conductivity measurements of their solutions in acetonitrile (~ $0.3 \text{ S m}^2 \text{ M}^{-1}$), indicates the formation of neutral complexes implying that the ligand molecules coordinate as anions.

At room temperature, the new Cu^{II} complexes exhibit paramagnetism (1.78–1.89 BM, Table 1) arising from one unpaired electron indicative of monomeric structure with strong covalent bonds [13]. In the case of [Cu(Et₂dtc)(oxime)] complexes, however, the observed decreased μ_{eff} values may be due to interactions between two copper molecules.

Tests of thin layer chromatography for all the mixed-ligand complexes under investigation, along with their analoguous binary complexes, $[Cu(dtc)_2]$ and $[Cu(oxime)_2]$, were carried out under exactly similar conditions, using CH_2Cl_2 as solvent and $CH_3COCH_3-CH_3OH-CHCl_3$ (40%-20%-40%) as eluent. The determined R_f values lie at an intermediate position between their constituent binary complexes suggesting that they are not equimolar mixtures of them but new species. Representative R_f values are given for the complexes 4, 8 and 16. $\{[Cu(Pipdtc)_2],$ [Cu(ppox)₂] and [Cu(Pipdtc)(ppox)]: 0.87, 0.61 and 0.81; $[Cu(Et_2dtc)_2]$, $[Cu(apox)_2]$ and $[Cu(Et_2dtc)(apox)]$: 0.86, 0.55 and $0.80; [Cu(Benz_2dtc)_2], [Cu(ppox)_2]$ and $[Cu(Benz_2dtc)(ppox)]: 0.83, 0.61 and 0.78].$

IR Spectra

The 2-hydroxyoxime and the dithiocarbamate ligands have the potential of a variety of coordinate modes depending upon steric hindrance, hydrogen bonding and electronic consideration. The position of the bands in the infrared spectra of the studied complexes can be utilized to provide information on the nature of the Cu-ligands bonds. A list of the most relevant infrared frequencies of the copper(II) complexes is given in Table 2. This includes absorptions due to the dithiocarbamate anion, to the 2-hydroxyoxime anion and to the copper(II) coordination bonds.

The thioureide band $v(S_2C \dots N)$ of the sodium dithiocarbamates about 1470 cm⁻¹ [14] shows a shift towards higher energies as a result of complexation and appears at 1480–1505 cm⁻¹ indicating increased bond order of the carbon-nitrogen bond. Besides, in the region 900–1020 cm⁻¹, the presence of a single strong band due to the stretching mode of the group CSS, causes evidence for the bidentate nature of the dtc anion through both sulfur atoms [4]. Moreover, evidence for the coordination bond Cu–S arises from the presence of a medium intensity band at 350– 380 cm⁻¹.

In the IR spectra of the 2-hydroxyoximes the stretching mode of the oximino hydroxyl group observed at $3360 \pm 30 \text{ cm}^{-1}$ as an intense broad band [1–3]. The variety of this band's position discloses the

influence of the substituents. In the mixed ligand copper(II) complexes, the former band appeared at significantly lower energies (about 300 cm⁻¹ comparing with the free ligands), indicative of the coordination through the nitrogen atom [15]. Evidence for this coordination also arised from the band at 1600 cm^{-1} due to v(C=N) and the bands in the region 965-1050 cm⁻¹ due to v(N-O), whereas in the free ligands appear at 1610 and 900–1000 cm^{-1} respectively [16, 17]. The bands of the ligands observed in the region $3200-3040 \text{ cm}^{-1}$ and $1410-1360 \text{ cm}^{-1}$ due to the stretching and to the in-plane O-H bending mode of the phenolic hydroxyl, respectively [18, 19], disappeared in the complexes indicating the replacement of the phenolic hydrogen by the copper atom. The bands originating from the C-O stretching vibration appeared at significantly higher frequencies in the region $1310-1370 \text{ cm}^{-1}$ as compared to the position 1245- 1285 cm^{-1} in the free hydroxyoximes giving evidence for the coordination of copper through the phenolic oxygen [20].

The medium intensity bands observed at $480-520 \text{ cm}^{-1}$ are potentially attributed to stretching vibrations of the Cu–N bonds. Assignment of the bands related to vibrations of the Cu–O is quite uncertain.

Electronic Excitation Spectra

The electronic excitation spectra of the chelates were studied in the visible and the near-infrared region, in the solid state (Nujol mulls) and in solution (CH_2Cl_2). In every case absorptions due to intraligand transi-

tions predominate at higher frequencies, while in the intermediate energy region of the spectra, two bands appeared at about 29,000 cm⁻¹ and at 27,000 cm⁻¹ due to excitations involving charge transfer. Credence to this arised from the comparison of the spectra of $[Cu(2-OHaryloxime)_2]$ and of $[Cu(dtc)_2]$ complexes, where the CT bands observed at 27,800 cm⁻¹ [2] and at 22,900 cm⁻¹ [21] respectively.

In the ligand field excitation spectra of the mixedligand complexes, two bands observed in the solid state, the one well defined, Band I (at $\sim 15,500$ cm⁻¹ for the [Cu(Pipdtc)(oxime)] and $[Cu(Benz_2dtc) \cdot$ (oxime)] complexes and at $\sim 14,500 \text{ cm}^{-1}$ for the $[Cu(Et_2dtc)(oxime)]$ complexes) and the other as a shoulder, Band II at ~ $19,000 \text{ cm}^{-1}$ (Table 2) suggesting square planar arrangement of the chromophore CuNOS₂, probably attributable to $d_{x^2 - y^2} \leftarrow d_{xy}$ and $d_{x^2-y^2} \leftarrow d_{xz, yz}$ transitions respectively. This is in agreement with other copper(II) chelates with squareplanar geometry of the chromophore CuS₄ or CuN₄ [21] and of the CuO_2N_2 chromophore [2, 22], where the observed d-d bands are fewer than the expected four bands. In solution, a broad absorption band observed in the visible region centered at $\sim 16,200 \text{ cm}^{-1}$ (Band I, Table 2) for all the complexes, indicating a shift to higher energies comparing with those observed in the solid state.

It is well known [4] that in the dialkyldithiocarbamate complexes of copper(II), there is a dominant tendency to form dimers in the solid state due to intermolecular interactions of the type $Cu-S\cdots Cu$, leading to a fifth coordination site of the copper atoms, with a

Table 2 Vibrational frequencies (ν/cm^{-1}) for selected absorption bands in the IR spectra and band maxima (d-d) in the electronic excitation spectra ($\tilde{\nu}/cm^{-1}$) of the [Cu(dtc)(oxime)] complexes

	Complex	$S_2 \cdots N$	CS	Cu–S	=N-OH	C-0	CuN	Band I ⊿E _{xv}	Band II(Sh) ⊿E _{xz}
1	[Cu(Pipdtc)(saox)]	1505	1020	355	3040	1340	475	15.570 ^N 16.310 ^c	<u> </u>
2	[Cu(Pindtc)(anox)]	1505	1020	355	3050	1370	520	15,500 [№] , 1.6210 ^c	19.270 ^c
ĩ	[Cu(Pindtc)(upox)]	1505	1020	355	3060	1313	540	15,450 [№] , 16,310 [°]	19.230 ^c
4	[Cu(Pipdtc)(npox)]	1505	1020	355	3060	1330	540	15.500 ^N , 16.310 ^c	18.970°
5	[Cu(Pipdtc)(ppox)]	1505	1020	345	3050	1335	540	15,380 ^N , 16,100 ^c	19.050°
6	[Cu(Pipdtc)(opox)]	1505	1020	355	3040	1350	540	15,620 ^N , 16,210 ^c	19.150 ^c
7	$[Cu(Et_2dtc)(saox)]$	1495	990	350	3000	1330	485	14,470 ^N , 16,000 ^c	_
8	$[Cu(Et_2dtc)(apox)]$	1480	990	345	3060	1312	445	14,860 ^N , 16,210 ^c	$19,120^{\circ}$
9	$[Cu(Et_2dtc)(mpox)]$	1495	990	350	3070	1315	440	14,600 ^N , 16,210 ^c	$19,010^{\circ}$
10	$[Cu(Et_2dtc)(ppox)]$	1495	990	350	3040	1323	470	14,490 ^ℕ , 16,210 ^c	$18,970^{\circ}$
11	$[Cu(Et_2dtc)(ppox)]$	1490	990	350	3040	1325	490	14,700 [×] , 16,210 [⊂]	19,050 ^c
12	$[Cu(Et_2dtc)(opox)]$	1490	900	350	3040	1325	490	14,790 [×] , 16,100 ^c	$18,940^{\circ}$
13	$[Cu(Benz_2dtc)(saox)]$	1490	970	380	3040	1348	510	15,360 [№] , 16,310 ^c	$18,970^{\circ}$
14	$[Cu(Benz_2dtc)(apox)]$	1480	980	375	3060	1315	435	15,340 [№] , 16,210 ^c	19,120 ^c
15	$[Cu(Benz_2dtc)(mpox)]$	1480	985	380	3060	1315	440	15,240 [№] , 16,100 ^c	19,230 ^c
16	$[Cu(Benz_2dtc)(ppox)]$	1480	985	380	3040	1325	440	15,290 [№] , 16,310 ^c	$19,120^{\circ}$
17	[Cu(Benz ₂ dtc)(bpox)]	1480	980	375	3040	1325	490	15,190 [×] , 16,100 ^c	$19,080^{\circ}$
18	[Cu(Benz ₂ dtc)(opox)]	1480	980	380	3045	1350	540	15,150 ^N , 16,100 ^c	18,690 ^c

[№]: Nujol; ^c: CH₂Cl₂

sqare pyramidal geometry, as it has been proved for the complex $[Cu(Et_2dtc)_2]$ [23, 24]. The axial interactions $(Cu \cdots S 2.85 \text{ Å})$ do not persist in solution where the complex is monomeric [25]. Thus, in the mixedligand complexes under investigation, the observed blue shift of the Band I in their solution spectra may be due to the elimination of such interactions resulting in the increase of the ligand field strength. The appreciably high blue shift in the case of the $[Cu(Et_2dtc)(oxime)]$ complexes (~14,500 cm⁻¹ in the solid state, while ~16,200 cm⁻¹ in solution), in combination with the reduced value of the magnetic moment (μ_{eff} ~1.70 BM, Table 1) suggest a possible dimerization of these complexes in the solid state.

ESR Spectra

The ESR spectra obtained in the solid state at room temperature and in frozen CH₂Cl₂ solution consisted of four ill-resolved resonance lines. However, the spectra of some [Cu(Pipdtc)(oxime)] complexes (a representative one is given in Figure 1 for [Cu(Pipdtc)(mpox)]) were sufficiently resolved to permit determination of components of the spin-Hamiltonian parameters. These spectra were analysed by computer simulation using throughout Lorenzian line shapes with different line widths. Isotope effects due to the natural occurance of ⁶³Cu and ⁶⁵Cu were taken into consideration and hyperfine-related second order correction in the resonance fields was applied employing the procedure of Chachaty [26]. The simulated spectra agreed satisfactorily with the observed ones and permitted the evaluation of the magnetic parameters. The magnetic parameters are summarised in Table 3 and support a square coplanar geometry, which is correlated with $d_{x^2 - y^2}$ ground state electron configuration [27]. The resulting CuNOS₂ chromophore (Scheme 2) possesses a C_v symmetry. Since however, the copper-oxygen and copper-sulfur bonds are approximately of the same polarizability and the



Fig. 1 ESR spectra of [Cu(Pipdtc)(mpox)] in the solid state at ambient temperature and in CH_2Cl_2 frozen solution



Scheme 2 Schematic diagram of the structure of the [Cu(Pipdtc)(oxime)] chelates

metal-to-ligand distance is in the range of 1.9–2.3 Å, as observed in square planar chelates with CuN_2O_2 or CuS_4 chromophores [28, 29], it could approximately assumed that the CuNOS₂ chromophore approaches a C_{2v} symmetry.

The consequencies of metal-ligand bond formation and electron delocalization from the ligand atoms to the copper(II) ion, and the effect of covalency on the coordination bonds can be estimated by calculating the in-plane bonding parameters α (σ -bonding) and β (π -bonding) encountered in LCAO theory [30–33].

Assuming negligibly small values of the overlap integral, S, the value of the parameter α^2 (or β^2) = 0.5 indicates essentially covalent bonding, while α^2 (or β^2) = 1 denotes completely ionic character.

The relations between the bonding and the magnetic parameters can approximately be expressed by the following equations:

$$g_{\parallel} \approx 2.0023 - 8\,\lambda\,\alpha^2\beta^2/\Delta E_{xy} \tag{8}$$

$$g_{\perp} \approx 2.0023 - 2\,\lambda\,\alpha^2 \beta'^2 / \Delta E_{xz} \tag{9}$$

$$A_{\parallel} = P[-\alpha^2(4/7 + \kappa_0) - (g_{\parallel} - 2) + 3/7(g_{\perp} - 2)]$$
(10)

$$A_{\perp} = P[\alpha^2 (2/7 - \kappa_0) + 11/14(g_{\perp} - 2)]$$
(11)

The spin-orbit coupling constant, λ , and the Fermi contact term, κ_0 , for the free Cu(II) ion is -828 cm⁻¹ and 0.43 respectively. For the free-ion dipole term, P, the value 360×10^{-4} cm⁻¹ has been calculated [32, 33]. ΔE_{xy} is the energy of the $d_{x^2 - y^2} \leftarrow d_{xy}$ excitation and the ΔE_{xz} is the energy of the $d_{x^2 - y^2} \leftarrow d_{xz}$, yz transition, which are evaluated from the electronic excitation spectra of the chelates under consideration.

The parameter α can be estimated from the copper hyperfine spectra by using the equations (3) and (4). The values of α^2 thus obtained are given in Table 3 and were used to estimate, from equations (1) and (2), the values of β^2 and β'^2 , which are a direct measure of the covalency of the in-plane and out-of-plane π bonding, respectively. For comparison purposes are also included, in the same Table, the results of studies for three copper(II) chelates with square planar geometry, which are related with the chelates under investigation. a) The bis(pyrrolidinedithiocarbamato)copper(II), [Cu(Pyrrdtc)₂] [4b]], a compound with CuS₄ chromophore, very much similar with the [Cu(Pipdtc)₂], b) the bis(salicylaldehyde-Me-imine)copper(II) [32]

Complex	g _{il} (±0.003)	$g_{\perp}(\pm 0.003)$	$-A_{\parallel} 10^4 (\pm 1)$ cm ⁻¹	$-A_{\perp} 10^4 (\pm 1)$ cm ⁻¹	α^{2} (±0.01)	β^2	β'^2
[Cu(Pipdtc)(ppox)]	2.116	2.054 2.056 ^s)	161	39	0.63	0.43	0.99
[Cu(Pipdtc)(mpox)]	2.119 2.166 ^s)	2.055 2.060 ^s)	144	33	0.58	0.47	1.09
[Cu(Pipdtc)(bpox)]	2.117 2.135 ^s)	2.053 2.054 ^s)	159	37	0.64	0.42	0.95
[Cu(Pyrrdtc) ₂] ^a)	2.110	2.020	144.8	30.5	Strong covalency	Moderate covalency	Moderate covalency
[Cu(Salicylaldimine)] ^b) [Cu(Me ₂ en)i-MNT] ^c)	2.200 2.145	2.045 2.076	185.0 184.3	21.0 35.0	0.76 0.83	0.72 0.39	0.91 1.02

 Table 3
 ESR and bonding parameters for [Cu(Pipdtc)(oxime)] and related chelates

^a) Ref. [4 b], ^b) Ref. [31], ^c) Ref [34], ^s) Solid state.

with CuN_2O_2 chromophore and c) the mixed-ligand chelate [Cu(Me₂en) i-MNT], where Me₂en = N,Ndimethylethylenediammine and i-MNT = 1,1-dicyano-2,2-ethylenedithiolate dianion, with CuN_2S_2 chromophore [34].

The bonding parameters (α^2 and β^2) derived from the ESR observables indicate appreciable in-plane covalency mainly due to the π bonding and less to the σ bonding, while the β'^2 values imply that the out-ofplane π bonding interaction are purely ionic.

Description of the Structure of Cu(ppox)₂

In the unit cell can be found two separated molecules of the complex. Details of crystal analysis, data collection and structure refinement are given in Table 4, together with the final values for the unit cell. Atomic

Table 4 Crystal data and structure refinement for $Cu(C_9H_{10}NO_2)_2$

Formula	$C_{18}H_{20}N_2O_4Cu$
Formula weight	391.90
Wavelength	0.71069 Å
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a	12.072(7) Å
b	5.204(2) Å
с	13.571(6) Å
β	103.72(1)deg.
Volume	828.2(7) Å ³
Z	2
Density (calculated)	1.571 Mg m ⁻³
F(000)	406
Independent reflections	1603 [R(int) = 0.0290]
Goodness-of-fit on F ²	1.050
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0311, wR_2 = 0.0769$
R indices (all data)	$R_1 = 0.0559, wR_2 = 0.0854$
Largest diff. peak and hole	0.385 and -0.223 e. Å ⁻³

positions and equivalent isotropic temperature factors for non hydrogen atoms are listed in Table 5. Interatomic distances and bond angles with their standard deviations are listed in Table 6.

As shown in Figure 2, each molecule consists of a copper atom and two deprotonated ppox ligands. The interatomic distances (Table 6) reveal that the copper atom is coordinated to two nitrogen and two oxygen atoms in a centrosymmetric distorted square-planar arrangement. The Cu–N bonds are appreciably longer than the Cu–O ones [1.949(2) Å and 1.882(2) Å respectively], similar to the distances observed in analogous copper complexes [28, 35–37] and in 2-OH propiophenoneoxime complexes of nickel [3] and palladium [38]. The best plane that encompasses the metal atom and formed by O(1), O(1[#]), N, N(1[#]) is expressed by the equation:

-16.7832(1)x - 20.5007(5)y + 22.3739(1)z = 0.

Table 5 Atomic coordinates $(\times 10^4)$ and equivalent isotropic displacement parameters $(\mathring{A}^2 \times 10^3)$ for non hydrogen atoms in Cu(C₉H₁₀NO₂)₂

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	у	Z	U(eq)
Cu	0	0	0	34(1)
O(1)	237(2)	2681(3)	957(1)	41(1)
O(2)	-2140(2)	-244(4)	-1420(1)	48(1)
N	-1562(2)	1120(4)	-565(2)	36(1)
C(1)	-1653(2)	4558(4)	586(2)	34(1)
C(2)	-507(2)	4359(5)	1157(2)	35(1)
C(3)	-123(3)	6072(6)	1965(2)	44(1)
C(4)	-838(3)	7842(5)	2240(2)	50(1)
C(5)	-1964(3)	7993(6)	1719(2)	51(1)
C(6)	-2351(2)	6398(5)	907(2)	44(1)
C(7)	-2138(2)	3019(5)	-318(2)	35(1)
C(8)	-3318(2)	3568(5)	-955(2)	42(1)
C(9)	-4217(2)	2081(6)	-576(2)	53(1)

Table 6 Selected interatomic distances [Å] and bond angles [deg] for non hydrogen atoms in Cu(C₉H₁₀NO₂)₂

the second secon	
Cu-O(1)	1.882(2)
Cu–O(1)#1	1.882(2)
Cu–N#1	1.949(2)
Cu–N	1.949(2)
O(1)–C(2)	1.326(3)
C(2) - C(3)	1.403(4)
C(2) - C(1)	1.420(4)
C(1) - C(6)	1.411(4)
C(1)-C(7)	1.466(3)
C(7)-N	1.297(3)
C(7) - C(8)	1.508(3)
C(8) - C(9)	1.519(4)
N-O(2)	1.398(3)
C(3) - C(4)	1.373(4)
C(4)-C(5)	1.378(4)
C(5) - C(6)	1.370(4)
O(2)-O(1)	2.568(3)
O(1)-Cu-O(1)#1	180.0
O(1)-Cu-N#1	88.60(8)
O(1)CuN	91.40(8)
N#1-Cu-N	180.0
C(2)–O(1)–Cu	129.0(2)
O(1)-C(2)-C(3)	117.6(2)
O(1)-C(2)-C(1)	123.8(2)
C(3)-C(2)-C(1)	118.6(2)
C(6)-C(1)-C(2)	117.2(2)
C(6)-C(1)-C(7)	118.7(2)
C(2)-C(1)-C(7)	124.1(2)
N-C(7)-C(1)	120.0(2)
N-C(7)-C(8)	119.2(2)
C(1)-C(7)-C(8)	120.8(2)
C(7)-C(8)-C(9)	111.3(2)
C(7) - N - O(2)	114.1(2)
C(7)–N–Cu	130.8(2)
O(2)-N-Cu	114.9(2)
C(4)-C(3)-C(2)	121.8(3)
C(3)-C(4)-C(5)	120.3(3)
C(6)-C(5)-C(4)	119.0(3)
C(5)-C(6)-C(1)	123.0(3)
O(2)-H(2)-O(1)	136.6(2)

Symmetry transformations used to generate equivalent atoms: #1-x, -y, -z



Fig. 2 Atoms drawing and labelling scheme of Cu(ppox)₂

Each ppox ligand is bonded through the oxime nitrogen atom and the deprotonated hydroxyphenyl oxygen forming a six-membered chelate ring. This chelate ring and the phenyl ring of the oxime almost lie on the previous plane and only the terminal carbon C(9) of the ethyl group is outside the oxime best plane at a distance 1.244(2) Å. The C(8)-C(9) bond of the ethyl group which is connected to the oxime ring has a slope of $63.92(2)^\circ$ with the best plane.

It is finally worthy to be mentioned that rather strong intra-molecular hydrogen bonds observed between the phenolic oxygen of one ppox ligand and the oximic hydrogen of the second ppox ligand

 $[O(2)-O(1^{\#}) = 2.58(3) \text{ Å}, O(2)-H(2)\cdots O(1^{\#}) = 1.909(3)\text{ Å}, O(2)-H(2)-O(1^{\#}) = 136.6(2)^{\circ}].$



Fig. 3 Packing of molecules in the unit cell of $Cu(ppox)_2$

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