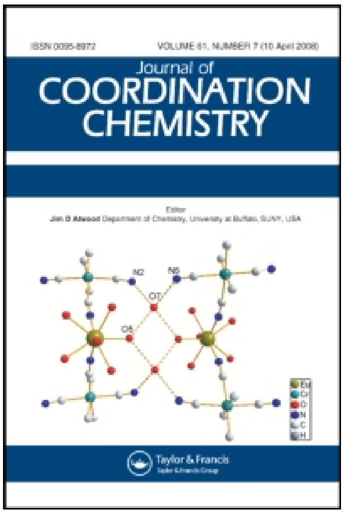

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UNSYMMETRICAL TETRADENTATE COMPLEXES OF COPPER (II)

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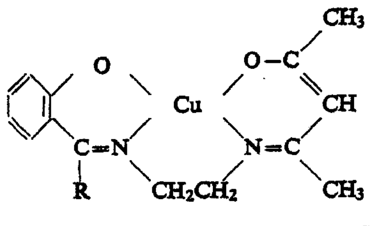
Four mixed tetradentate Cu(II) chelates were prepared by reacting a copper salt, acety acetone, and ethylenediamine with salicylaldehyde, *o*-hydroxyacetophenone, *o*-hydroxypropiophenone, and *o*-hydroxybutyrophenone, respectively. The I.R., optical, and E.S.R. spectra were obtained and discussed with regard to the expected bonding changes and/or those predicted by a model molecular orbital calculation for mixed ligand complexes.

INTRODUCTION

A combined experimental and theoretical investigation of the electronic structure and chemical bonding of low symmetry transition metal complexes is in progress in our laboratory in order to extend the knowledge of the dependence of bonding upon symmetry. This is considered important since many spectroscopic theories have been derived and/or tested mainly for cases of relatively high symmetry while many complexes of practical use such as industrial catalyst systems and biological complexes are of low symmetry. In previous papers we have reported the preparation and characterization of mixed acetylacetonate type complexes of Cu(II)[1,2] and have reviewed four different approaches for the determination of Cu(II) bonding and structure parameters from electron spin resonance spectroscopy data.[3] In the present paper we are extending the study to mixed complexes with two completely different ligand types. In order to avoid the problems of a possible solution equilibrium between the mixed and symmetrical complexes we decided to take advantage of the reaction of bis complexes with ethylenediamine to form a tetradentate complex. The unsymmetrical chelates, then, have the general structure:



$R = H, CH_3\ C_2H_5, n - C_3H_7$

EXPERIMENTAL

The abbreviations used in this paper are: Hsal, salicylaldehyde; Hhap, *o*-hydroxyacetophenone; Hhpp, *o*-hydroxypropiophenone; Hhbp, *o*-hydroxybutyrophenone; Hacac, acetylacetone; en, ethylenediamine.

Preparation of the Complexes

Bis(acetylacetone)ethylenediiminocopper(II), Cu(acac)₂en The ligand was prepared according to the method described by McCarthy, *et. al.*[4] The complex was also prepared according to the same authors except that a small excess of $CuCO_3 \cdot Cu(OH)_2$ was employed instead of pure $Cu(OH)_2$. The product was recrystallized from cyclohexane to give dark purple crystals, mp 135–137° (lit. 137°).[5]

Bis(salicylaldehyde)ethylenediiminocopper(II), Cu(sal)₂en The ligand was synthesized according to the method described by Griswold.[6] The complex was presented by dissolving the ligand in ethanol and adding an aqueous solution of a stoichiometric amount of cupric acetate. After heating and stirring the solution for 30 minutes, the olive-green product was collected by filtration and air-dried, mp 298–301°dec (lit. 315–317°).[7]

Bis(o-hydroxyacetophenone)ethylenediiminocopper(II), Cu(hap)₂en The ligand was prepared by refluxing stoichiometric amounts of en and Hhap in methanol. The solution, upon cooling to room temperature, yielded a yellow precipitate which was washed with cold methanol. To prepare the tetradentate complex, a suspension of $CuCO_3 \cdot Cu(OH)_2$ in $CHCl_3$ was added to a $CHCl_3$ solution of the ligand (mp, 194.5–196°), and the reaction mixture was heated at 50° with stirring until the solutions turned a dark brown color. The cooled (0°) solution yielded a brown precipitate which was washed with hot methanol, recrystallized from $CHCl_3$, and washed with hot benzene, and dried in an oven at 80°. The final product was pink-brown in color, mp 289–294°.

Bis(o-hydroxypropiophenone)ethylenediiminocopper(II), Cu(hpp)₂en The yellow ligand (mp 131–132.5°) was prepared in a manner similar to that described above for $Cu(Hap)_2en$. The complex was prepared by 3.22 g (0.01 mole) of the ligand with 1.11 g (0.005 mole) of $CuCO_3 \cdot Cu(OH)_2$ in acetone for 24 hours. The gray-purple precipitate, after a hot petroleum ether and hot ligroin wash, was recrystallized from hot acetone and air dried, mp 264–267°dec.

Bis(o-hydroxybutyrophenone)ethylenediiminocopper(II), Cu(hbp)₂en The ligand was prepared in a manner similar to that described above for $Cu(Hap)_2en$. The complex was also synthesized according to the method described above; the brown-purple product was washed with hot methanol and dried at 80° for 4 hours, the last trace of solvent being removed under high vacuum (mp 260–263°dec).

Salicylaldehydeacetylacetoneethylenediiminocopper(II), Cu(acac)(sal)en To a solution of 11.2 ml (0.1 mole) of salicylaldehyde and 10.01 ml (0.1 mole) of acetylacetone in 200 ml benzene at 70°, was added 6.6 ml (0.1 mole) en and the reaction mixture was refluxed for 1.5 hours. The benzene was removed by evaporation, and the resulting oily ligand concentrate was dissolved in 150 ml of acetone. After addition of 11.05 g (0.05 mole) $CuCO_3 \cdot Cu(OH)_2$, the reaction mixture was stirred for 1.5 hours at room temperature. During that time, a dark green solid precipitated from the dark purple reaction solution. The green precipitate was collected on a filter and washed with acetone as the washings were concentrated by evaporation under suction, a dark purple solid precipitated. This precipitate was collected, washed twice with hot cyclohexane and air dried, mp 184°dec. This dark purple compound is the desired mixed tetradentate complex Cu(acac)(sal)en, whereas the remaining purple solution contains mainly $Cu(acac)_2en$, and the residual green solid is entirely $Cu(sal)_2en$.

o-Hydroxyacetophenoneacetylacetoneethylenediiminocopper(II), Cu(acac)(hap)en This mixed tetradentate complex was prepared in a manner similar to that described for Cu(acac)(sal)en, using 13.6 ml (0.1 mole) of Hhap. The final product, which is a dark grayish-purple in color, was purified by recrystallization from acetone, and gave a melting point of 201–205°, dec.

o-Hydroxyproprophenoneacetylacetoneethylenediiminocopper(II), Cu(acac)(hpp)en The ligand mixture was prepared by the addition of 1.67 ml (0.025 mole) of en to a mixture of 3.75 g (0.025 mole) of Hhpp and 2.58 ml (0.025 mole) of Hacac, without solvent. The viscous mixture was dissolved in acetone and an acetone solution of 5.0 g (0.025 mole) of cupric acetate was added. After stirring the reaction mixture for 24 hours at room temperature, the solvent was removed, and the resulting solid was chromatographed on a Florisil column using a 50/50 (V/V) mixture of CH_2Cl_2-acetone. The first band contains $Cu(acac)_2en$, while the second band, which closely follows the first, contains the mixed tetradentate complex. The other symmetrical tetradentate formed in the reaction, $Cu(hpp)_2en$, moves only very slowly down the column under these conditions. The solvent from the second band was removed under a stream of nitrogen gas, yielding a purple solid, mp 198, dec.

o-Hydroxybutyrophenoneacetylacetoneethylenediiminocopper(II), Cu(acac)(hbp)en The mixed complex was prepared in a manner similar to that described above for Cu(acac)(sal)en, using 16.4 g (0.1 mole of Hbp, and 20.0 g (0.1 mole) of cupric acetate. The final product gave a melting point of 159°, dec.

Methods of Characterization

Infrared spectra of the complexes were recorded in the CsBr region as Nujol nulls on a Perkin–Elmer Model 221 spectrophotometer equipped with a CsBr interchange, and also on a Perkin–Elmer Model 521 grating spectrophotometer. Electronic absorption spectra were obtained on a Perkin–Elmer Model 450 spectrophotometer in the visible and ultraviolet regions on $CHCl_3$ and CH_3CN solutions of the complexes. ESR studies were carried out on a Strand-Magnion, Varian hybrid spectrometer on 10^{-2}–10^{-3} M solutions of the complexes in $CHCl_3$, which was purified immediately before use by passing it through an activated for the same series as above. A comparison of the visible spectra of the mixed and symmetrical complexes is given in Figure 2.

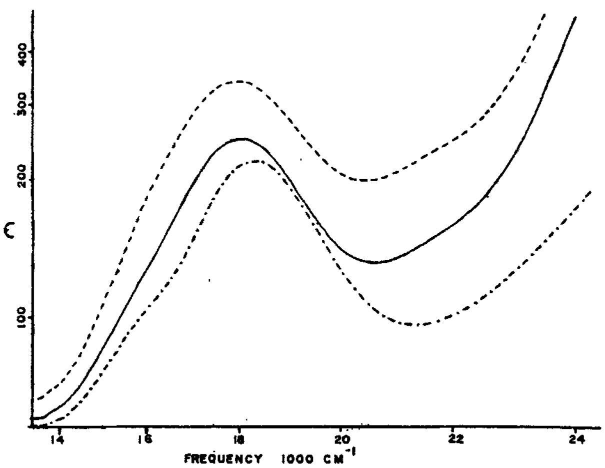


FIGURE 2 The CH_3CN solution visible spectra of $Cu(acac)_2en$ —·—·— Cu(acac)(hap)en ——, and $Cu(hap)_2en$ — — — — —.

The optical spectra of $Cu(acac)_2en$ and $Cu(sal)_2en$ have been the subject of a number of papers[10–17]. Chakrovorty and Basu[13] reported three peaks in the polarized single crystal optical spectra of Cu(acac) $_2en$ at 19,800 cm^{-1}, 18,300, and 16,300. They also performed a Gaussian analysis on the alcohol solution spectrum and found that the peaks are at 19,600 cm^{-1}, 18,300, and 16,700. Ferguson[17] studied the polarized single crystal spectra of $Cu(sal)_2en$ and reported a y-polarized band at 17,900 cm^{-1} and a x-polarized shoulder at 20,800 cm^{-1}. Downing and Urbach[18] utilizing circular dichroism made the following assignments for the d-d transitions in $Cu(acac)_2$ propane-1, 2-diamine: $z^2 \rightarrow xy$ at 15,950 cm^{-1}; x^2–$y^2 \rightarrow xy$ at 18,150 and $xz \rightarrow xy$ at 21,690. For $Cu(sal)_2$propane-1, 2-diamine they were not able to observe the z^2 transition, but the x^2–$y^2 \rightarrow xy$ transition was assigned at 16,950 and the $xz \rightarrow xy$ was assigned at 20,700. The ordering of the levels and the decrease in energy observed in going from the acac complex to the sal complex is consistent with our calculated behavior, but the relative oscillator strengths are not. The theoretical oscillator strengths of above 3×10^{-3} give values for the extinction coefficients around 200; this is the correct order of magnitude However, the theoretical ratio of the $Cu(sal)_2en$ to $Cu(acac)_2en$ extinction coefficients is only 1.02 while the experimental value is around 2. Perhaps the discrepancy is due to the idealized symmetry used in the theoretical calculations or to our neglect of vibronic and intensity borrowing mechanisms.[18] The second discrepancy is that the most intense peak is predicted to be predominantly z^2 while the experimental assignments have assumed it to be predominantly x^2–y^2.

The data for the ultraviolet spectra are given in Table V. Typical spectra for the mixed and symmetrical complexes are given in Figure 3.

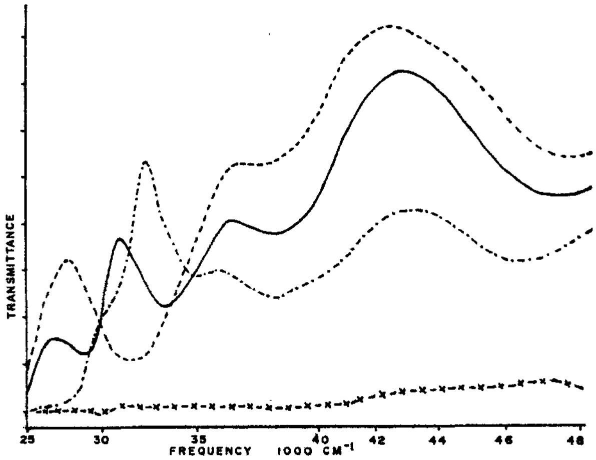


FIGURE 3 The CH_3Cn solution U.V. spectra of $Cu(acac)_2en$—·—·— Cu(acac)(hap)en——, and $Cu(hap)_2en$ — — — — —.

As a first step in the analysis of the spectra we determined which bands involved predominantly ligand to ligand transitions by comparing the copper spectra with those for the free ligand and the corresponding zinc complex. The zinc complex has a filled shell thus eliminating any possibility of low lying ligand to metal charge transfer transitions (low lying high intensity metal to ligand transitions are not expected for this type of copper complex).

By this comparison one can definitely assign the 32,700 cm^{-1} band and the shoulder at about 30–31,000 as having significant ligand–ligand character. These bands are very similar to bands in $Cu(acac)_2$ that have been assigned as predominantly C=C π to C=O π transitions in the acetylacetone ring. However, from our calculations it appears that they involve more of the C=N π orbital than of the C=O π orbital.

In the $Zn(acac)_2en$ spectrum there is a low intensity shoulder at $\approx$27,000 cm^{-1}. In $Cu(acac)_2$ a similar band has been assigned by Avdeev and Zakharov[19] as a ligand to xy transition and by Cotton and Wise[20] as a x^2–y^2 or yz to π *transition. The appearance of this band in the d^{10} Zn(acac)$_2$en supports Cotton and Wise's assignment; although, of course, both types of transitions could fall in this region. The rest of the Zn(acac)$_2$en U.V. spectrum to 50,000 cm^{-1} is clean with only the slowly rising tail of a peak above 50,000 evident. For this reason the peaks in Cu(acac)$_2$en at ≈36,800 and 43,000 can be assigned as ligand to metal transitions. Our molecular orbital calculations, see Table VI, are consistent with this analysis.

The U.V. spectra of H$_2$(sal)$_2$en and Zn(sal)$_2$en indicate that there will be four intense ligand–ligand transitions in the Cu(sal)$_2$en spectrum. Unfortunately these lines cover most of the U.V. region leaving only a small window between ≈30,000

TABLE

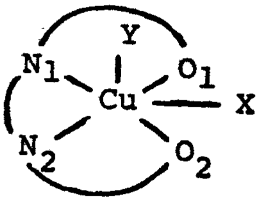
Calculated molecular orbital

Atom	Atomic Orbital	I[a]	II	III	I	II	III
ΔE[b]		0.0	0.0	0.0	19,881	18,532	17,213
Cu	z^2	0.0000	0.0043	0.0000	0.7828	−0.9239	−0.9608
	xz	0.0	0.0	0.0	0.0	0.0	0.0
	x^2–y^2	0.0000	−0.0005	0.0000	0.5797	−0.3116	−0.1731
	yz	0.0	0.0	0.0	0.0	0.0	0.0
	xy	0.8726	−0.8754	0.8785	−0.0000	−0.0074	0.0000
	4s	0.0000	0.0012	−0.0000	0.0620	−0.0723	−0.0742
	4Pz	0.0	0.0	0.0	0.0	0.0	0.0
	4Px	−0.0000	−0.0085	−0.0000	−0.0061	0.0032	0.0016
	4Py	−0.0310	0.0309	−0.0307	0.0000	0.0012	−0.0000
O$_1$[c]	S	−0.0907	0.0856	−0.0829	0.0011	0.0010	0.0001
	Pz	0.0	0.0	0.0	0.0	0.0	0.0
	Px	0.1841	−0.1724	0.1749	−0.0540	0.0451	0.0418
	Py	0.1785	−0.1728	0.1700	−0.0053	0.0246	0.0368
O$_2$	S	0.0907	−0.0878	0.0829	−0.0011	−0.0000	0.0001
	Pz	0.0	0.0	0.0	0.0	0.0	0.0
	Px	−0.1841	0.1868	−0.1749	−0.0540	0.0479	0.0418
	Py	0.1785	−0.1755	0.1700	0.0053	−0.0305	−0.0368
N$_1$	S	0.1255	−0.1182	0.1140	0.0045	−0.0047	−0.0042
	Pz	0.0	0.0	0.0	0.0	0.0	0.0
	Px	0.2813	−0.2666	0.2733	0.1799	−0.1543	−0.1412
	Py	−0.2910	0.2827	−0.2822	−0.0146	0.0617	0.0778
N$_2$	S	−0.1255	0.1212	−0.1140	0.0045	−0.0041	−0.0042
	Pz	0.0	0.0	0.0	0.0	0.0	0.0
	Px	−0.2813	0.2885	−0.2733	0.1799	−0.1620	−0.1412
	Py	−0.2910	0.2899	−0.2822	0.0146	−0.0569	−0.0778

[a] I is Cu(acac)$_2$en, II is Cu(acac)(sal)en, and III is Cu(sal)$_2$en.

[b] ΔE is the energy difference in cm^{-1} between the particular molecular orbital and the highest energy occupied orbital.

[c] The spacial arrangement is with the sal group in the mixed complex along the +Y axis.



cm^{-1} and ≈35,000 where Cu(sal)$_2$en ligand to metal transitions could be assigned with confidence, if present. Our calculations on Cu(sal)$_2$en predict ligand to metal transitions at 31,400 cm^{-1} and 33,900; however, no experimental bands are observed in this region. Downing and Urbach,[18] utilizing circular dichroism, did not detect any absorptions in this region for the similar Cu(sal)$_2$ propane-1, 2-diamine complex.

In the mixed complexes two peaks with potential bonding information can be identified with the corresponding peaks in the spectra of the non-mixed complexes. The unresolved doublet (≈31,000 cm^{-1} and ≈32,000) in Cu(acac)(sal)en most likely is the 30–31,000 and 32,500 C=C π to C=N π doublet in Cu(acac)$_2$en. The decrease in the π–π^* separation in the mixed complex can be interpreted as a decrease in the amount of metal π bonding

IV

coefficients and energies

I	II	III	I	II	III	I	II	III
19,960	18,631	17,369	20,429	19,076	17,839	20,464	19,182	17,863
0.5826	−0.3162	−0.1780	0.0	0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.0	−0.0016	0.5951	0.0010	−0.9749	−0.7743	−0.9783
−0.7918	0.9311	0.9678	0.0	0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.9710	0.7693	0.9755	−0.0016	0.5963	0.0010
0.0000	−0.0052	−0.0000	0.0	0.0	0.0	0.0	0.0	0.0
0.0465	−0.0250	−0.0139	0.0	0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0000	−0.0024	−0.000	0.0062	0.0057	0.0059
0.0061	−0.0073	−0.0071	0.0	0.0	0.0	0.0	0.0	0.0
0.0000	0.0020	0.0000	0.0	0.0	0.0	0.0	0.0	0.0
0.0009	0.0002	−0.0010	0.0	0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.0	−0.0775	−0.1054	−0.0734	0.0843	0.0161	0.0783
0.0184	−0.0349	−0.0398	0.0	0.0	0.0	0.0	0.0	0.0
−0.0744	0.0628	0.0619	0.0	0.0	0.0	0.0	0.0	0.0
0.0009	−0.0024	−0.0010	0.0	0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0778	0.0090	0.0732	0.0841	0.1150	0.0784
0.0184	−0.0320	−0.0398	0.0	0.0	0.0	0.0	0.0	0.0
0.0744	−0.0730	−0.0619	0.0	0.0	0.0	0.0	0.0	0.0
0.0014	0.0008	0.0003	0.0	0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.0	−0.1930	−0.0425	−0.1765	−0.1783	−0.2374	−0.1658
−0.0285	0.0695	0.0965	0.0	0.0	0.0	0.0	0.0	0.0
−0.1492	0.1163	0.1217	0.0	0.0	0.0	0.0	0.0	0.0
0.0014	−0.0010	0.0003	0.0	0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.1924	0.2623	0.1768	−0.1789	−0.0279	−0.1654
−0.0285	0.0881	0.0965	0.0	0.0	0.0	0.0	0.0	0.0
0.1492	−0.1530	−0.1217	0.0	0.0	0.0	0.0	0.0	0.0

since the mixing of the metal π orbitals would result in a greater stabilization of the bonding π orbital and/or destabilization of the antibonding orbital. However, the second peak with potential bonding information, the 28,000 cm^{-1} peak of Cu(sal)$_2$en, also shifts to lower energy (27,000) in Cu(acac)(sal)en. From circular dichroism studies[18, 22] on the similar (sal)$_2$propylenediamine complexes we would expect that this peak is a closely spaced doublet due to π to π* transitions involving the sal C=N group. The decrease in separation of both the acac and sal π and π* levels in going from Cu(acac)$_2$en and Cu(sal)$_2$en to Cu(acac)(sal)en is unexpected. It may be due to the separation between the two types of π systems. In the symmetrical complexes the energies of the two π systems are identical and maximum mixing can occur. This mixing would stabilize the π bonding orbital and destabilize the π* orbital. When the two ligands are different, the two π systems are at different energies and less mixing (i.e. less stabilization and destabilization) will occur. Of course it also could be due to a decrease in the amount of metal bonding with the ligand π orbitals due to a distortion in the system or simply less d electron density available for π bonding. Our molecular orbital calculations predict that the energy of the first π to π* transition for the mixed complex would be intermediate between the energies of the non-mixed systems. However, the calculation does not consider the total ligand systems and, therefore, may be excessively dependent on the contribution of the metal orbitals.

TABLE V

Bands in the ultraviolet region for the symmetrical and mixed complexes in CH_3CN

Compound[a]	ν(cm^{-1})	ϵ(10^{-3} l mole^{-1}cm^{1})
Cu(acac)$_2$en	≈26,500(sh)	≈0.1
	≈30,000(sh)	0.8
	32,500	2.1
	34,000(sh)	1.5
	36,000	1.0
	43,000	1.5
Cu(hap)$_2$en	27,500	1.1
	36,500	2.1
	42,500	5.3
	45,000(sh)	≈3.8
Cu(acac)(hap)en	27,000	0.45
	31,000	1.3
	36,500	1.5
	43,000	3.8

[a] The spectra of the other two series of complexes were within experimental error the same as for this series.

ESR Spectra The ESR data are given in Table VII. Except for the two complexes with sal groups, these compounds give unusually high resolution ESR spectra, see Figure 4. Presumably, the reason for the broad peaks when a sal group is present is the additional hyperfine splitting with the proton on the azomethine carbon. Maki and McGarvey[23] have been able to resolve the proton splitting from this position for bis-salicyladehyde-imine Cu(II) by the use of dilute single crystals.

TABLE VI

Calculated energies and oscillator strengths for the ligand to metal charge transfer transitions[i,j]

molecule	$B_2 \rightarrow B_2$	$A_1 \rightarrow B_2$	$B_2 \rightarrow B_2$	$A_1 \rightarrow B_2$	$B_2 \rightarrow B_2$
Cu(acac)$_2$en	28.0(.0236)[a]	33.8(.151)[c]	36.7(.186)[c]	43.3(.143)[a]	58.5(.0371)[g]
Cu(acac)(sal)en	27.0(.0224)[a, b]	32.6(.142)[c, d]	35.3(.176)[c, e]	41.5(.136)[a, f]	57.4(.0366)[g, h]
Cu(sal)$_2$en	26.0(.0216)[a]	31.4(.134)[c]	33.9(.167)[c]	39.8(.130)[a]	56.4(.0361)[g]

[a] Principal contribution fron nitrogen p_y orbitals.

[b] Ratio of sal p_y nitrogen to acac p_y nitrogen contribution is 1.02 greater sal than acac.

[c] Principal contribution from nitrogen p_x orbitals.

[d] Ratio of sal p_x nitrogen to acac p_x nitrogen contribution is 1.02.

[e] Ratio of sal p_x nitrogen to acac p_x nitrogen contribution is 0.94.

[f] Ratio of sal p_x nitrogen to acac p_x nitrogen contribution is 0.98.

[g] Principal contribution from oxygen p_y orbitals.

[h] Ratio of sal p_y oxygen to acac p_y oxygen contribution is 1.01.

[i] Energies in 10^3 cm^{-1}. The oscillator strengths are enclosed in brackets.

[j] For simplicity the C_{2v} nomenclature has been used for all three compounds even though the mixed compound is actually C_s symmetry.

Of the three experimental ESR parameters it is felt that the nitrogen hyperfine splittings are the most dependable for determining the relative covalancy of the non-mixed complexes. For the mixed complexes it is expected that the observed nitrogen splitting is the superposition of two slightly inequivalent splittings. Our theoretical calculations predict a nitrogen splitting of 9.16 gauss for $Cu(acac)_2en$, 7.53 for $Cu(sal)_2en$, 8.46 for the acac nitrogen of Cu(acac)(sal)en and 8.18 for the sal nitrogen.

From the copper hyperfine splittings it is apparent that the Cu(acac)(sal)en complex is unique among the mixed complexes, and from the g values it is probable that $Cu(sal)_2en$ is unique among the sal series. The sal complex is known to form a chloroform adduct with the chloroform hydrogen bonded to an oxygen.[24] However, the optical spectrum of the sal complex is similar to the spectra of the substituted sal complexes and there does not appear to us to be any reason why this hydrogen bonding would be unique to the unsubstituted sal complexes. Since the copper hyperfine splitting is expected to increase as the amount of 4s electron density increases, the five gauss increase in the Cu(acac)(sal)en value over the other mixed complexes could be due to a greater distortion from planar symmetry which would mix in more 4s character. About 0.5% more 4s character would be required. Again, it is difficult to see why the sal complex would be more distorted; in fact, we would have predicted the opposite. Futher studies of the frozen ESR spectra are planned in an effort to explain this behavior.

TABLE VII

ESR data for the mixed and symmetrical tetradentate chelates

Compound[a]	g[b]	ACu[c]	A^N[d]
$Cu(sal)_2en$	2.0946	86.1	not resolved
$Cu(hap)_2en$	2.0936	86.2	14.0
$Cu(hpp)_2en$	2.0936	86.2	13.8
$Cu(hbp)_2en$	2.0935	86.1	13.6
Cu(acac(sal)en	2.0931	86.2	not resolved
Cu(acac)(hap)en	2.0930	81.7	14.4
Cu(acac)(hpp)en	2.0928	81.5	14.2
Cu(acac)(hbp)en	2.0930	81.1	14.2
$Cu(acac)_2en$	2.0921	85.1	14.7

[a] In alcohol free $CHCl_3$.

[b] ±0.0005

[c] In 10^4 cm^{-1}; ±0.5

[d] In gauss; ±0.3

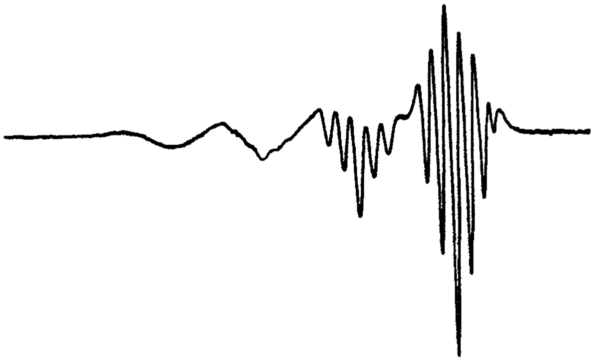


FIGURE 4 ESR spectra of a $CHCl_3$ solution of $Cu(hbp)_2en$.

Molecular orbital calculations For the theoretical calculations the extended Huckel method was used. The calculations used the arithmetic mean approximation to calculate the off-diagonal elements, H_{ij}, with K having a value of 2.00. The values of the Coulomb integrals, H_{ii}, and the orbital exponents that were used are: Cu(3d), −11.5 E.V. and 3.14; Cu(4s), −3.10 and 1.42; Cu(4p), −0.30 and 1.42; 0(2s), −33.8 and 1.892; 0(2p), −17.4 and 1.64; N(2s), −25.56 and 1.875; and for N(2p), −13.19 and 1.65 respectively. The calculation was identical to the calculation by Cotton, Harris, and Wise[25] on a $Cu(acac)_2$ type complex except that only the copper, two oxygens, and the two nitrogens were included. The internuclear distances used are 1.97 A° and 2.01 for the Cu–O and Cu–N distances in the sal complex[26] and 1.94 and 1.97 for the Cu–O and Cu–N distances in the acac complex.[27] The molecular orbital energies and coefficients are given in Table IV. The sigma bond to the ligands, xy, is calculated to be of intermediate covalency for the mixed complex. Some mixing of the in-plane π, x^2–y^2, and the z^2 orbital is predicted with the greatest amount in the $Cu(acac)_2en$ complex, presumably due to the short metal-ligand bond lengths. The mixed complex is predicted to display a different type of out of plane π bonding from the two symmetrical complexes. The xz and yz orbitals mix and form one π orbital with the sal oxygen and the acac nitrogen and another with the sal nitrogen and the acac oxygen.

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