E.s.r. and Optical Spectral Properties of Copper(II) Complexes with Schiff-Base Ligands Derived from *o*-Aminobenzaldehyde

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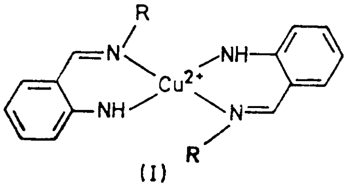
Optical and e.s.r. spectra have been measured for a number of copper(II) complexes with Schiff-base ligands derived from *o*-aminobenzaldehyde. Absorption bands at *ca.* 39 500 and 24 000 cm^{-1} are proposed as $\pi \longrightarrow \pi^*$ transitions, the latter being split into two components in complexes with quadridentate ligands. Bands at *ca.* 19 000 and 14 000 cm^{-1} are attributed to transitions within the copper 3*d* shell. An absorption near 22 000 cm^{-1} is assigned to a $\pi \longrightarrow d_{xy}$ transition. The optical and e.s.r. parameters of the complexes are consistent with planar co-ordination of the copper ion except for *NN'*-1,3-propylenebis(*o*-aminobenzylideneiminato)copper(II), in which a small tetrahedral distortion of the co-ordination sphere is indicated. The strong ligand field exerted by the *o*-aminobenzylideneimine ligands precludes additional axial co-ordination of solvent molecules.

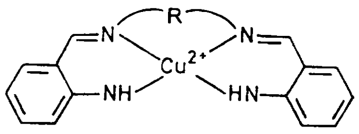
EXTENSIVE studies on co-ordination complexes with salicylideneimine ligands have revealed a diversity of stereochemical arrangement [1] arising from steric [2] and electronic [3] effects within the molecules. Although such complexes of copper(II) with ligands derived from salicylaldehyde are well characterized the analogous complexes with Schiff bases of *o*-aminobenzaldehyde have received less attention. The structural and electronic properties of this latter series are clearly of interest as an indication of the role of the donor-atom set in determining physicochemical characteristics.[4-6] In the present paper the preparation of several *o*-aminobenzylideneimine complexes and their electronic absorption and e.s.r. spectra are described. A single-crystal *X*-ray diffraction study of one of the complexes, *NN'*-1,2-propylenebis(*o*-aminobenzylideneiminato)copper(II), has been previously reported.[7]

EXPERIMENTAL

Free ligands and complexes were prepared by methods already reported.[5,6,8-10] The bidentate ligand (I) is abbreviated as abNR following ref. 6 and the quadridentate ligand (II) as abR. The compounds [Cu(aben)], [Cu(abpn)], [Cu(abtn)], and [Cu(abNMe)] were isolated in crystalline form but [Cu(abphn)] and [Cu(abbphn)] could only be prepared as amorphous powders. Attempted syntheses of $[Cu(abNEt)]$, $[Cu(abNPr^i)]$, and $[Cu(abNBu^t)]$ yielded only intractable red tars.


(I)

R = Me: [Cu(abNMe)]
R = Et: [Cu(abNEt)]
R = Bu^t: $[Cu(abNBu^t)]$
R = Pr^i: $[Cu(abNPr^i)]$


(II)

R = $[CH_2]_2$: [Cu(aben)]
R = $[CH_2]_3$: [Cu(abtn)]
R = $CH(Me)CH_2$: [Cu(abpn)]
R = *o*-phenylene: [Cu(abphn)]
R = 2,2'-biphenylene: [Cu(abbphn)]

Electronic spectra of the complexes were recorded with a Cary-14 spectrophotometer. Solvents were of spectroscopic purity and were dried over molecular sieves. Stoppered cells were used with appropriate solution-handling techniques to minimize hydrolysis of the compounds. Solid-state spectra were obtained with KBr discs or Nujol mulls.

E.s.r. spectra were recorded with a Varian E-12 spectrometer equipped with 100 kHz modulation within a Varian multipurpose cavity and a variable-temperature accessory. *g*-Values were measured relative to DPPH contained in a capillary inserted into the sample tube. Spectra were recorded in 40% chloroform–60% toluene glasses at 123 K. Solvents were of analytical grade and were dried over calcium hydride. The stabilizing ethanol was not removed from the chloroform.

RESULTS AND DISCUSSION

The electronic absorption bands of the *o*-aminobenzylideneimine ligands listed in Table 1 correspond closely with those of the analogous salicylideneimine Schiff bases and accord, where ranges are common, with those already reported.[6] However, the anion of the ligands could not be produced, even in sodium methoxide, making more difficult the assignment of intra-ligand bands in the spectra of the complexes. In salicylideneimine systems the ligand anion bands are not significantly perturbed upon formation of the copper complex whereas the free ligand bands may undergo large shifts.[11]

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[1] R. H. Holm, G. W. Everett, and A. Chakravorty, *Progr. Inorg. Chem.*, 1966, **7**, 83.

[2] T. P. Cheeseman, D. Hall, and T. N. Waters, *J. Chem. Soc.* (*A*), 1966, 685.

[3] (*a*) B. J. Hathaway and D. E. Billing, *Co-ordination Chem. Rev.*, 1970, **5**, 143; (*b*) E. N. Baker, D. Hall, and T. N. Waters, *J. Chem. Soc.* (*A*), 1970, 400, 406.

[4] M. Green and P. A. Tasker, *Inorg. Chim. Acta*, 1971, **5**, 65.

[5] B. M. Higson and E. D. McKenzie, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 209.

[6] B. M. Higson and E. D. McKenzie, *J.C.S. Dalton*, 1972, 269.

[7] D. Hall, T. N. Waters, and P. E. Wright, *J.C.S. Dalton*, 1973, 1508.

[8] P. Pfeiffer, Th. Hesse, H. Pfitzner, W. Scholl, and H. J. Thielert, *J. prakt. Chem.*, 1937, **149**, 217.

[9] M. Green and P. A. Tasker, *J. Chem. Soc.* (*A*), 1970, 2531.

[10] M. Green and P. A. Tasker, *J. Chem. Soc.* (*A*), 1970, 3105.

[11] T. N. Waters and P. E. Wright, *J. Inorg. Nuclear Chem.*, 1971, **33**, 359.

However the similarity of the spectra of *o*-aminobenzylideneimine and salicylideneimine ligands is helpful and allows some band assignments to be made. The band at *ca.* 29 000 cm^{-1} in the *o*-aminobenzylideneimines is thus attributed to a $\pi \longrightarrow \pi^*$ transition involving molecular orbitals which originate from the azomethene group and benzene ring, as in the salicylideneimines.[12,13] In accord with the assignment in anilines [14] and in benzaldehyde Schiff bases [15] the band at *ca.* 44 000 cm^{-1} is assigned to the benzenoid $^1L_a\pi \longrightarrow \pi^*$ transition. The origin of the absorption at *ca.* 39 000 cm^{-1} is not clear, having been variously attributed to a $\pi \longrightarrow \pi^*$ benzenoid band [16] and to intramolecular charge transfer in other aromatic Schiff bases.[15] The weak band at *ca.* 24 000 cm^{-1} is assigned to an $n \longrightarrow \pi^*$ transition involving the lone-pair electrons of the azomethene nitrogen atom and the π^* orbital associated with the azomethene group. The observed solvent shifts (Table 1) are in accord with such an assignment and may be rationalized by the argument proposed by Bosnich for the analogous salicylideneimine ligands.[12]

Assignment of the electronic spectra of the complexes is made on the assumption of planar molecules with the *z*-axis perpendicular to the molecular plane. The present studies provide no means of distinguishing between a d_{xy} or $d_{x^2-y^2}$ ground state. However, it is generally accepted that for square-planar complexes with ligands of the present type which have potential π-bonding the copper d_{xy} orbital is the one singly occupied.[3a]

The *o*-aminobenzylideneimine complexes studied herein exhibit a pattern of absorption bands (Table 2) similar to those of their salicylideneimine analogues.[11] Bands at 43 900 and 29 800 cm^{-1} in the solution spectrum of [Cu(abNMe)] which are absent from the solid-state spectrum (KBr disc, Nujol mull) arise from partial hydrolysis of the complex. Although [Cu(abNMe)] is very susceptible to decomposition in this way complexes derived from quadridentate ligands appear to be more stable.

Since replacement of a hydroxy-substituent in aromatic systems by a substituent of lower electronegativity, such as an amino-group, is known to destabilize the highest occupied π-orbital, whereas the π^*-orbitals are relatively unaffected,[17] it seems reasonable to assume that intra-ligand $\pi \longrightarrow \pi^*$ bands in the spectra of *o*-aminobenzylideneimine complexes will be at somewhat lower energies than the corresponding bands of salicylideneimine complexes. On this basis the bands at *ca.* 25 000 and 24 000 cm^{-1} in the spectra of the copper(II) complexes with quadridentate *o*-aminobenzylideneimine ligands are assigned to the two components of the azo-

TABLE 1

Absorption bands (in cm^{-1}) of *o*-aminobenzylideneimine ligands

o-Aminobenzaldehyde [a]						
n-Hexane:	$\bar{\nu}$		39 100	38 000sh	28 100	
	ε		5600	3400	4700	
NN'-Ethylenebis(*o*-aminobenzylideneimine)						
Dioxan:	$\bar{\nu}$		39 100sh	33 300sh	29 000	
	ε		10 000	2000	6500	
Ethanol:	$\bar{\nu}$	44 100	39 200sh	33 700	28 900	24 100sh
	ε	39 000	16 000	3600	5800	1400
Ethanol–sodium methoxide:	$\bar{\nu}$		38 800sh	33 300sh	29 000	
	ε		12 000	2700	5300	
NN'-1,3-Propylenebis(*o*-aminobenzylideneimine)						
Ethanol:	$\bar{\nu}$	43 500	38 500		29 200	
	ε	36 000	14 200		10 900	

[a] J. C. Dearden and W. F. Forbes, *Canad. J. Chem.*, 1960, **38**, 1837.

sh = shoulder.

TABLE 2

Absorption bands (in cm^{-1}) of *o*-aminobenzylideneimine complexes in chloroform solution

[Cu(aben)]	$\bar{\nu}$	39 500	33 600		25 300sh	24 000	21 700sh	18 900sh	14 700
	ε	57 000	11 000		6700	13 000	4000	400	330
[Cu(abpn)]	$\bar{\nu}$	39 500	33 400		25 400sh	24 000	21 700sh	19 200sh	14 700
	ε	60 000	11 000		8000	12 000	3700	430	340
[Cu(abtn)]	$\bar{\nu}$	39 800	33 300		25 000sh	23 600	22 200sh	18 000sh	12 850
	ε	53 000	9000		9000	11 000	7000	800	320
[Cu(abphn)]	$\bar{\nu}$	37 700	30 600	29 000		24 200	20 900		14 800sh
	ε	32 000	16 000	13 500		14 500	15 000		400
[Cu(abNMe)]	$\bar{\nu}$	39 700	33 300sh	29 800 *		23 600		16 100sh	10 400
	ε	19 000	6000	4400		7000		300	160
[Ni(aben)]	$\bar{\nu}$	39 100	31 400		27 400sh		20 800		
	ε	59 000	25 000		8800		6500		

* Free ligand band due to partial hydrolysis of complex. A further free ligand band occurs at 43 900 cm^{-1} (ε = 45 000 l mol^{-1} cm^{-1}) in ethanol solution.

sh = shoulder.

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[12] B. Bosnich, *J. Amer. Chem. Soc.*, 1968, **90**, 627.

[13] J. Murrell, *Tetrahedron Suppl.*, 1963, **2**, 277.

[14] S. Besnainou, *J. Chimie Physique*, 1970, **67**, 1825.

[15] M. Ashraf El-Bayoumi, M. El-Aasser, and F. Abdel-Halim, *J. Amer. Chem. Soc.*, 1971, **93**, 586, 590.

[16] K. K. Chatterjee and B. E. Douglas, *Spectrochim. Acta*, 1965, **21**, 1625.

[17] H. H. Jaffe and M. Orchin, 'Theory and Applications of Ultraviolet Spectroscopy,' Wiley, London, 1962, p. 248.

methene $\pi \longrightarrow \pi^*$ band, split by exciton interactions, as in the analogous salicylideneimine complexes.[12] Such exciton splitting is, however, expected to be absent from the spectra of complexes with bidentate ligands,[12] and in accord with theory, only a single $\pi \longrightarrow \pi^*$ band is observed at 23 600 cm^{-1} with [Cu(abNMe)]. The shoulder of moderate intensity at *ca.* 21 000 cm^{-1} appears to arise from charge transfer involving ligand and metal orbitals but detailed study of its spectral characteristics is not possible because it is only observed as an inflection in the more intense $\pi \longrightarrow \pi^*$ envelope. The absorption is tentatively assigned as $\pi \longrightarrow d_{xy}$ in accord with its low energy and relatively low intensity.[18] Since the π-orbitals in *o*-aminobenzylideneimine ligands are expected to be of higher energy than the corresponding orbitals in salicylideneimines the $\pi \longrightarrow d_{xy}$ band might be expected to be at lower energy in complexes of the former; in the planar salicylideneimine copper(II) complexes the corresponding $\pi \longrightarrow d_{xy}$ transition is hidden beneath the first $\pi \longrightarrow \pi^*$ band.[19]

A further band may be assigned by comparison with the spectrum of [Ni(aben)] (prepared as in ref. 9). The very intense absorption band at 39 100 cm^{-1} clearly corresponds to the band at this energy in the spectra of the copper(II) complexes, suggesting that this absorption arises from an internal ligand transition. The very high intensity of the band indicates that it arises, in part at least, from the ^1L_a benzenoid transition, perturbed by complexation and shifted to lower energy. Similarly the band at *ca.* 33 000 cm^{-1} in the spectra of the copper complexes may also correspond to an internal ligand transition or it may arise from charge transfer, possibly of the $\sigma \longrightarrow d_{xy}$ type found in several salicylideneimine complexes.[11] An unambiguous assignment cannot, at present, be given. Reference to the spectrum of [Ni(aben)] is of no help since it is difficult to ascertain whether this band is absent for the nickel complex or merely shifted in energy, perhaps contributing to the absorption at 31 400 cm^{-1}.

The bands of very low intensity in the visible region are assigned to $d \longrightarrow d$ transitions. The similarity of the ligand-field spectra of [Cu(aben)], [Cu(abpn)], and [Cu(abphn)] suggests an identical co-ordination environment in these complexes. However, when in [Cu(abtn)] the number of atoms in the di-imine bridge is increased, the prominent ligand-field band is shifted to lower energy, a similar effect having been reported for the corresponding nickel(II) and cobalt(II) complexes.[9,10] This reduction in ligand-field strength may arise from steric effects due to the increased length of the bridging moiety or from distortion to a flattened tetrahedral co-ordination geometry of the type found in *NN'*-1,3-propylenebis(*o*-hydroxyacetophenoneiminato)copper(II).[20]

There is no significant difference between the ligand-field spectrum of each *o*-aminobenzylideneimine complex in chloroform solution, in pyridine solution, or in the solid state (Table 3). In particular, the lack of spectral perturbation by pyridine suggests that the copper ion in these complexes has no tendency to undergo additional axial co-ordination. The same conclusion has been reached by Higson and McKenzie.[6] This persistent planarity could arise from either a strong ligand field [21] or from steric hindrance to pyridine co-ordination.[22] Since the analogous salicylideneimine complexes clearly exhibit no steric hindrance to binding by the solvent,[23] the only apparent explanation in steric terms requires that an axially bridged dimeric species be maintained in solution. Such an explanation can be discounted, however, since crystalline [Cu(abpn)] is notable for the complete absence of close axial approaches to the copper ion,[7] and because strong dimeric associations would probably be reflected in the e.s.r. spectrum, as in [Cu(sal)$_2$(en)].[24] The lack of spectral perturbation in co-ordinating solvents is therefore taken to indicate that *o*-aminobenzylideneimine ligands exert a stronger ligand field than their salicylideneimine counterparts. A similar conclusion has been reached from studies on *o*-aminobenzylideneimine complexes of nickel(II) and cobalt(II).[9,10]

TABLE 3

Effect of solvent on ligand-field bands (in cm^{-1})

Complex	$\bar{\nu}$ (chloroform)	$\bar{\nu}$ (pyridine)	$\bar{\nu}$ (solid state)
[Cu(aben)]	14 710	14 930	
	18 900sh	18 500sh	
[Cu(abpn)]	14 730	14 930	14 700 (Nujol mull)
	19 200sh	19 200sh	*a*
[Cu(abtn)]	12 850	12 840	12 700 (Nujol mull)
	18 000sh	18 200sh	*a*
[Cu(abNMe)]	10 400	10 300	10 400 (KBr disc)
	16 100sh	16 000sh	16 700sh
[Cu(sal)$_2$(en)] *	17 700	16 700	17 500 (Nujol mull)

* The salicylaldimine analogue of [Cu(aben)].

sh = shoulder.

[a] The weak shoulder in the solution spectrum was not detected in the mull.

TABLE 4

E.s.r. parameters

Complex	$g_{\parallel}$	$g_{\perp}$	$\frac{10^4\lvert A_{\parallel}\rvert}{cm^{-1}}$	$\frac{10^4\lvert A_{\perp}\rvert}{cm^{-1}}$
[Cu(aben)]	2·152	2·048	206	24
[Cu(abpn)]	2·153	2·046	205	26
[Cu(abtn)]	2·170	2·049	187	24
[Cu(abNMe)]	2·190		156	

The spin Hamiltonian parameters for the *o*-aminobenzylideneimine complexes are summarized in Table 4. Values of $g_{\parallel}$ and $\lvert A_{\parallel}\rvert$ were measured directly from the

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[18] C. K. Jorgensen, 'Absorption Spectra and Chemical Bonding in Complexes,' Pergamon Press, Oxford, 1962, p. 146ff.

[19] G. A. Bowmaker, T. N. Waters, and P. E. Wright, unpublished results.

[20] K. Iida, I. Oonishi, A. Nakahara, and Y. Komiyama, *Bull. Chem. Soc. Japan*, 1970, **43**, 2347.

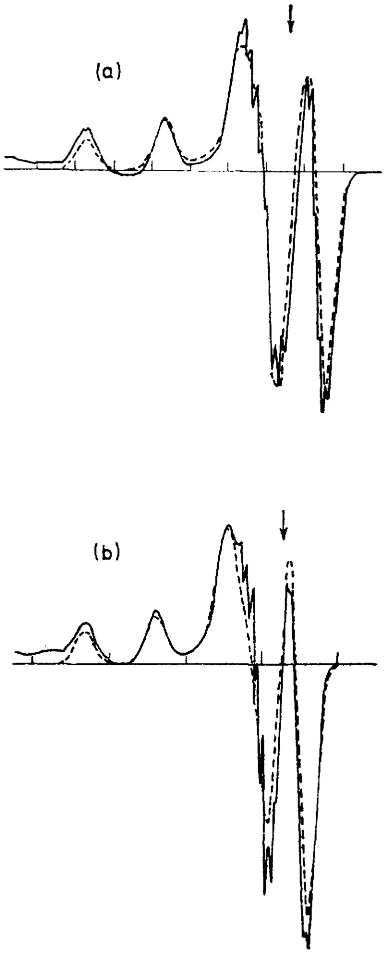
[21] H. C. Freeman in 'The Biochemistry of Copper,' eds. J. Peisach, P. Aisen, and W. E. Blumberg, Academic Press, London, 1966, p. 77.

[22] S. Yamada, E. Ohno, Y. Kuge, A. Takeuchi, K. Yamanouchi, and K. Iwasaki, *Co-ordination Chem. Rev.*, 1968, **3**, 247.

[23] J. M. Waters and T. N. Waters, *J. Chem. Soc.*, 1964, 2489.

[24] G. O. Carlisle and W. E. Hatfield, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 633.

spectra. Approximate values of $g_\perp$ and $|A_\perp|$ were estimated and adjusted until the simulated spectrum was in close visual agreement with experiment. The computer program allowed for variation of the line width with orientation, assuming an axially symmetric line-width tensor,[25] but did not include ligand superhyperfine coupling. Calculated spectra were in excellent agreement with experiment (Figure) except for [Cu(abNMe)] which is partly hydrolyzed under the conditions of the experiments and for which no reliable values of $g_\perp$ and $|A_\perp|$ can be given. The ligand superhyperfine splitting evident in the spectra of the quadridentate Schiff-base complexes was not sufficiently resolved to allow more than the facile deduction that the unpaired electron is delocalized onto the ligand.



Measured (——) and simulated (— — —) e.s.r. spectra for (a) [Cu(abpn)] and (b) [Cu(abtn)]

Both the optical and e.s.r. spectra of [Cu(aben)], [Cu(abpn)], and [Cu(abphn)] are clearly consistent with a square-planar co-ordination geometry. Further, the complexes again show evidence of having remained four co-ordinate, even in donor solvents such as pyridine. For the complex [Cu(abtn)], however, the prominent ligand-field band is at lower energy and the value of $g_\parallel$ is larger and that of $|A_\parallel|$ is smaller than for the planar complexes. Such observations are consistent with a slight tetrahedral distortion [19] of the co-ordination square. A similar distortion is reflected in the optical and e.s.r. parameters of the salicylaldimine analogue [19] and has been demonstrated for the related complex, *NN'*-1,3-propylenebis(*o*-hydroxyacetophenoneiminato)-copper(II), by *X*-ray diffraction.[20] This result is of considerable interest in view of the suggestions that *o*-aminobenzylideneimine complexes of nickel(II) and cobalt(II) are square planar, even when this would appear to be sterically unlikely.[4,9,10] The occurrence of a tetrahedral distortion in [Cu(abtn)] is thus surprising since copper(II) generally resists a tetrahedral distortion more than the transition metal ions [26] mentioned above. The conclusion from the spectral data is, however, clear.

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[25] T. S. Johnson and H. G. Hecht, *J. Mol. Spectroscopy*, 1965, **17**, 98.

[26] E. E. Castellano, O. J. R. Hodder, C. K. Prout, and P. J. Sadler, *J. Chem. Soc.* (*A*), 1971, 2620.