# ELECTRONIC ABSORPTION BANDS IN SALICYLALDIMINE COMPLEXES OF ZINC(II)

A. C. BRAITHWAITE and T. N. WATERS Chemistry Department, University of Auckland, New Zealand

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Abstract—The electronic absorption spectra of Schiff base complexes of the  $d^{10}$  metal ion,  $Zn^{2+}$ , and the  $d^0$  ions  $Mg^{2+}$ ,  $Ca^{2+}$  and  $Al^{3+}$ , are presented to clarify assignments previously made for similar Cu(II) compounds. We find a general agreement except for a band at ca. 41,000 cm<sup>-1</sup> which consistently appears in the spectra and cannot, therefore, be the  $\sigma \rightarrow 3d$  transition proposed earlier. Several possible assignments are discussed.

## **INTRODUCTION**

INTEREST, both practical and theoretical, has long centred on the problem of assigning electronic absorption bands in several copper(II) systems [1-5]. This is especially true for complexes involving acetylacetone and its derivatives, where several sets of assignments have been proposed, the most detailed for bis(dipivaloylmethanido)copper(II)[3]. More recently the copper(II) salicylaldimine complexes, which bear a considerable resemblance to those of acetylacetone systems, have been investigated [6]. To clarify the assignments put forward we present here the electronic absorption spectra of several zinc(II) salicylaldimine complexes, the filled *d*-levels of the zinc(II) ion promising more simple spectra and useful comparison with copper(II). A further extension to study the spectra of complexes containing metal ions with empty *d*-levels is also presented.

## **EXPERIMENTAL**

## Preparative

The Schiff base ligands were prepared by addition of a methanolic solution of the appropriate amine, in slight excess, to a methanolic solution of the required salicylaldehyde followed by recrystallisation from methanol. Bis(salicylaldehydato)zinc(II) (I) was prepared by addition of salicylaldehyde (2.44g) in a methanolic KOH solution (1.12g) in methanol. Considerable difficulty was experienced in purifying the sample and contamination with zinc hydroxide proved impossible to eliminate entirely because of the instability of the complex towards hydrolysis (see later). The salicylaldimine-type complexes, bis(salicylaldiminato)zinc(II)[7] (II), bis(N-methylsalicylaldiminato)zinc(II)[8] (III), NN'-ethylenebis(salicylaldiminato)zinc(II)[9] (IV), bis(N-methyl-3-methoxysalicy-zinc(II) (V), bis(N-methyl-3-methoxysalicy-zinc(II) (VI), bis(N-methyl-3-

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laldiminato)zinc(II) (VII), and bis(N-isopropylsalicylaldiminato)zinc(II) [10] (VIII), were prepared by documented methods or extensions thereof.

The magnesium(II) complexes bis(salicylaldehydato)magnesium(II)[7] (IX) and NN'-ethylenebis-(salicylaldiminato)magnesium(II)[11] (X) and the corresponding calcium(II) complexes were prepared by reported methods. The salicylaldehyde complex of aluminium(III) (XI) was prepared by a modification of the method of Mehrotra and Mehrotra[12], the complex being precipitated by addition of methanol to the reddish oil first obtained and then dried in a vacuum. Analysis suggested that by this method the complex Al(sal)<sub>2</sub>OMe, or more likely the dimer Al<sub>2</sub>(sal)<sub>4</sub>(OMe)<sub>2</sub> with bridging oxygen atoms, had been formed. (Found: C, 60.62; H, 4.28; Al, 8.79. Alsal<sub>3</sub> requires C, 65.50; H, 3.78; Al, 6.74. Alsal<sub>2</sub>OMe requires C, 60.00; H, 4.36; Al, 8.98%.)

The ethylenediamine derivative (XII) was prepared by addition of ethylenediamine (0.62g) to a hot suspension of the salicylaldehyde complex (3.0g) in pyridine. The suspension quickly dissolved and deposited a yellow powder.

#### Spectra

Spectra were obtained with a Cary Model 14 spectrophotometer using stoppered cells. Solvents were of spectroscopic grade, being routinely dried over molecular sieves immediately before use with more rigorous drying being undertaken in many instances. Solid state spectra were measured recorded for samples mounted in potassium bromide discs. The spectra results of the new ligands are presented in Table 1, and for the complexes in Tables 2 and 3. Those in the latter tables have, where possible, been obtained in dioxan solution. Effects due to change of solvent are thus eliminated. Initially it was found that there were inconsistencies in the results, a problem traced to hydrolysis of the complexes in solution. Bands corresponding to the ligand spectra in Table 1 were found to varying degrees in the spectra of some of the zinc(II) complexes but could be eliminated through the use of very dry solvents. The spectra were then consistent with those obtained in the solid state from potassium bromide discs. Appropriate steps were routinely taken thereafter to minimise the effect of hydrolysis and the data for the zinc(II) complexes, in Table 2, have no significant ligand contribution.

## RESULTS

Zinc(II), being a  $d^{10}$  ion, exhibits no  $d \rightarrow d$  bands in the electronic spectra of its complexes and also shows no charge transfer bands of the type ligand  $\rightarrow 3d$ -

	Dioxan		Ethanolic KOH	
	$\overline{\nu}$ (cm <sup>-1</sup> )	$\epsilon$ (m <sup>2</sup> mole <sup>-1</sup> )	$\overline{\nu}$ (cm <sup>-1</sup> )	$\epsilon$ (m <sup>2</sup> mole <sup>-1</sup> )
N-methyl-5-chloro-salicylaldimine	45,000	2950	42,700	4320
	39,600	840	38,200	1940
	30,700	430	25,800	1660
N-methyl-3,5-dichloro-salicylaldimine	45,000	4280	42,400	3670
	38,400	1470	36,200	830
•	30,300	360	25,800	790
N-methyl-3-methoxy-salicylaldimine	44,000	1840	42,400	1090
	39,200	700	37,000	260
· · · ·	30,300	300	25,000	350
	23,400	60		

Table 1. Absorption spectra of ligands and anions\*

\*For the spectra of other ligands see Ref. [6].

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I†	$\overline{\nu}$	47,000	42,200	37,000		26,500	
	ε	5100	2400	10	590	510	
П	$\overline{\nu}$	45,000	40,300	36,	200	26,600	
	£	2860	6430	2	060	1300	
III	$\overline{\nu}$	44,400	41,700	38,600	37,000	27,200	
	ε	3700	2310	900	1290	1080	
	$\overline{\nu}$	44,300	42,000	36,	800	28,400	24,800
	(KBr	disc)					
IV	$\overline{\nu}$	43,700	40,800	37,	000	27,800	
	e	4770	3530	1	730	1730	
	$\overline{\nu}$	44,400	42,200	37,	900	27,700	25,500
	(KBr	disc)					
v	$\overline{ u}$	44,200	41,300	38,400	36,800	26,600	
	ε	3890	2320	890	630	630	
VI	$\overline{\nu}$	43,100	40,600	37,200		26,700	
	E	3200	3000	1670		1360	
VII	$\overline{\nu}$	42,200		36,200		26,600	
	e	3510		1	580	680	
	$\overline{\nu}$	42,900		36.	,200	26,400	22,600
	(KBr	disc)					
VIII	$\overline{\nu}$	44,200	41,300	36.	,800	27,100	
	ε	3680	4120	1	810	1250	
	$\overline{\nu}$	44,400	41,200	36.	,800	26,700	
	(KBr	disc)					

Table 2. Absorption spectra of the zinc(II) complexes\*  $(\bar{\nu} \text{ in cm}^{-1}; \epsilon \text{ in m}^2 \text{mole}^{-1})$ 

\*All spectra obtained in dioxan solution unless otherwise indicated. †Spectra in methanol solution.

Alumini	um(III) (	complexes					
XI	$\overline{\nu}$	46,500	41,800	39,100	36,400	30,800†	26,300
	ε	6600	1040	3460	660	1000	3500
	$\overline{\nu}$	45,000	42,000	37,200			25.400
	(KBr	disc)					
XII	$\overline{\nu}$	45,700	41,700	38,500	36,200	31,200†	27,500
	E	4020	2600	1900	610	610	570
Magnesi	um(11) c	omplexes			·		
IX	$\bar{\nu}$	46,000	42,200	38,700		30,700†	26,500
	ε	4860	2660	2320		300	800
Х	$\overline{\nu}$	43,900	40,800	37,500			27,800
	e	3300	3020	1460			1000

Table 3. Absorption spectra of $d^0$ metal complexes*
(units as in Table 2)

\*All spectra obtained in dioxan soln. unless otherwise indicated.

 $\dagger$ This band is attributed to a ligand contribution but could not be eliminated from the spectrum.

metal-orbital. Such  $\sigma \to 3d$  transitions have been assigned for the copper(II) complexes, i.e. in bis(dipivaloylmethanido)copper(II)<sup>3</sup>-48,000 ( $d_{yz} \to \pi^*$ ), 40,000 ( $\sigma \to 3d_{xy}$ ), 34,600, 32,300 ( $\pi \to \pi^*$  doublet), 26,600 cm<sup>-1</sup> ( $3d \to \pi^*$ ) and bis(N-methylsalicylaldiminato)copper(II)<sup>6</sup>-49,500 ( $d \to \pi^*$ ), 43,300 ( $\pi \to \pi^*$ ), 41,300 ( $\sigma \to 3d_{xy}$ ), 36,900 ( $\pi \to \pi^*$ ), 33,600 ( $\sigma \to 3d_{xy}$ ), 27,800 cm<sup>-1</sup> ( $\pi \to \pi^*$ ) and should therefore be absent from analogous compounds containing zinc(II).

Comparison of the spectra of the zinc(II) complexes with the corresponding spectra of the ligand shows, as for the copper(II) complexes, that the "ligand" orbitals are relatively unaffected by complex formation and that the three bands common to the anions can be identified at similar energies in the complexes. These bands, ca. 43,000, 38,000 and 26,000 cm<sup>-1</sup>, can be identified as  $\pi \rightarrow \pi^*$  bands as for the copper(II) complexes [6]. Comparison with the spectra of the latter also verifies, as expected, that bands below 20,000 cm<sup>-1</sup> are  $d \rightarrow d$  transitions [13], there being no corresponding bands in the spectra of zinc(II) complexes. The assignment of the 34,000 cm<sup>-1</sup> band as a  $\sigma \rightarrow 3d$  transition in copper(II) compounds is strengthened by the absence of a similar band when zinc is the metal. The 25,000 cm<sup>-1</sup> peak, tentatively assigned as a  $3d \rightarrow \pi^*$  transition in the corresponding copper(II) complexes [6, 13, 14] also seems to be absent from the spectra of the zinc(II) complexes although it may be the cause of a slight asymmetry in the low energy  $\pi \rightarrow \pi^*$  band of IV, VI and VII when methanol is used as solvent. Circular dichroism studies suggest that this low energy  $\pi \rightarrow \pi^*$  band suffers Davydov splitting [15], an asymmetry more noticeable in the solid state spectra [16, 17]. Thus the assignment of this peak can be neither verified nor disputed; if present for all the zinc(II) and copper(II) complexes, as it should be if a  $d \rightarrow \pi^*$  transition, it must be quite small and hidden under the low energy  $\pi \rightarrow \pi^*$  band appearing at approximately 27,000 cm<sup>-1</sup>.

The band that can be more seriously questioned is that at approximately  $41,000 \text{ cm}^{-1}$  which should disappear for zinc(II) complexes if it is the  $\sigma \rightarrow 3d$  transition assigned to it. It appears, however, in the spectra of all the zinc(II) complexes except VII, where the intense band usually appearing at about 44,000 cm<sup>-1</sup> shifts to 42,200 cm<sup>-1</sup> and probably hides the transition at 41,000 cm<sup>-1</sup>, which is usually only a shoulder under the best circumstances. The assignment as a  $\sigma \rightarrow 3d$  transition also implies that shifts are to be expected for different stereochemistries, but this does not appear to be in evidence either, although it must be noted that it is difficult to deduce the exact position of a peak which normally appears as a shoulder.

To assist in this problem the spectra of some selected  $d^0$  metal complexes, namely those of aluminium(III), magnesium(II) and calcium(II), were studied. Arguments based on the lack of ligand field stabilisation energies suggest that magnesium(II) and calcium(II) should form tetrahedral Schiff base complexes

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<sup>13.</sup> B. J. Hathaway, D. E. Billing and R. J. Dudley, J. chem. Soc. (A), 1420 (1970); R. J. Dudley, R. J. Fereday, B. J. Hathaway and P. G. Hodgson, J. chem. Soc. Dalton 1341 (1972).

<sup>14.</sup> J. Ferguson, J. chem. Phys. 34, 1609 (1961).

with bidentate ligands as does zinc(II)[18] but with electronic properties reflecting empty, rather than full, *d*-levels. Unfortunately the calcium(II) complexes are highly susceptible to hydrolysis in solution and cannot be used with any confidence for assignment studies. The magnesium(II) complexes, although still susceptible to hydrolysis, yield suitable spectra in very dry solvents, consistent with the observation that this ion shows stronger complex formation with several substituted salicylaldehydes than does calcium(II)[19], although values are still considerably weaker than those for nickel(II). The same trend seems likely to hold for the salicylaldimines. The aluminium(III) complexes are also subject to hydrolysis, with the added complication of being insoluble in many solvents.

The aluminium(III) and magnesium(II) complexes yield spectra that are very similar to those for the corresponding zinc(II) complexes, as can be seen from Table 3. Except in the spectra of X a ligand contribution is always observed, even in the very dry solvents, and these are assigned as such in Table 3. The results confirm the three  $\pi \rightarrow \pi^*$  assignments as these do not change for the different metal ions. The absence of a band at  $34,000 \text{ cm}^{-1}$  in complexes of magnesium(II), aluminium(III), or zinc(II) also supports this assignment as a  $\sigma \rightarrow 3d$  transition in the copper(II) complexes. No verification of the band assigned as a  $3d \rightarrow \pi^*$ transition in several copper(II) complexes is possible, although asymmetry in the low energy  $\pi \rightarrow \pi^*$  band for some of the spectra of the zinc(II) complexes, and an absence of this asymmetry for the d<sup>0</sup> metal complexes, suggest that its assignment could be correct. Thus all bands are accounted for except one, that at 41,000 cm<sup>-1</sup>, which appears in the spectra of the magnesium(II) and aluminium(III) complexes as well as for the zinc(II) complexes, and is found at a relatively constant energy throughout. This is not predicted for a charge transfer band, which would be expected to suffer energy changes in different stereochemical situations, and would certainly vary with different metal ions where a different "metal orbital" is involved each time. Its specification as a charge transfer process is thus discounted.

Reassignment poses several problems, however. The band is not present in the spectra of the ligand, or the anion of the ligand, suggesting that it does not involve purely ligand orbitals. The remaining option of extensive metal-ligand orbital mixing to destroy the assumption implicit in all the assignments, namely the retention of the essential electronic character of metal ion and ligand on complex formation, does not seem tenable. The bands of the ligand anion remain in the spectra of the complex and are relatively unchanged by different metals, neither observation supporting the assumption of complete orbital mixing.

It is unfortunate that the band, although large ( $\epsilon = 4300 \text{ m}^2 \text{mole}^{-1}$  in the ininstance of VIII where it is best resolved), is generally seen as a shoulder and cannot therefore have its energy correlated with changes to the ligands. In so far as we have been able to make such observations they do suggest that the transition is little affected by substituents on the benzene ring and is also unresponsive to the presence of co-ordinating solvents. The one positive observation is that the

<sup>18.</sup> R. H. Holm, G. W. Everett, Jr. and A. Chakravorty, Prog. Inorg. Chem. 7, 82 (1966).

<sup>19.</sup> K. Clarke, R. A. Cowen, G. W. Gray and E. H. Osborne, J. chem. Soc. 245 (1963).

band is absent from o-aminobenzylideneimine complexes [20] where all the donor atoms are nitrogens.

Since the transition is confined to complexes we assume, in the light of the above, that it is intra-ligand which is only "allowed" when a metal is present. It further seems likely that it is a transition which involves an oxygen orbital particularly. In valence bond terms it can be seen that the phenolate oxygen atom will rehybridise to an  $sp^2$  system (roughly) on complex formation so that the assumption of a changed electronic distribution and a new transition in the presence of a metal ion is plausible.

We were conscious at this point of literature reports of bands in the same region in acetylacetonato complexes of copper(II)[21, 22] (see Table 4) which

Complex	Band positions (cm <sup>-1</sup> )	Medium	
Tris(acetylacetonato)cobalt(III)	43,900, 38,400, 30,000	KBr disc*	
	43,900, 38,900	Solution [17]	
Bis(acetylacetonato)copper(II)	41,300, 34,000	Solution [17]	
Bis(dipivaloylmethanido)copper(II)	48,600, 40,000, 34,600, 32,300,		
	26,600	Solution [5]	
N,N'-ethylenebis(acetylacetoneiminato)copper(II)	44,100, 39,100, 36,200, 32,000,		
	29,600, 26,700	Solution [18]	
N,N'-ethylenebis(acetylacetoneiminato)nickel(II)	42,500, 37,000, 33,000, 30,700,		
	28,300, 27,000	Solution*	
Aquo-bis(acetylacetonato)zinc(II)	35,100, 32,800	Solution*	
	35,200	Solution [17]	
	37,400, 34,500, 31,600	KBr disc*	
Acetvlacetone anion	34,600	Solution [17]	

Table 4. Absorption spectra o	f several acety	lacetone comp	lexes*
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\*Present work.

indicated that the transition could be common, and essentially confined, to coordinated, trigonally-hydridised, oxygen atoms. There was, however, no evidence for the absorption in zinc(II) or nickel(II) acetylacetonates [21] but in view of the expected ease of hydrolysis of these compounds we repeated measurements in very dry methanol, or in the solid state, for aquo-bis (acetylacetonato)zinc(II) and N,N'-ethylenebis(acetylacetoneiminato)nickel(II). Pertinent results are listed in Table 4 and we interpret these as indicating that the 41,000 cm<sup>-1</sup> absorption is a feature of salicylaldimine ligands alone. The band at *ca*. 40,000 cm<sup>-1</sup> in the copper (II) acetylacetonates is confirmed as being the  $\sigma \rightarrow 3d$  transition deduced from molecular orbital calculations by its varying position in different compounds (42,500-39,100 cm<sup>-1</sup>) and its absence from aquo-bis(acetylacetonato)zinc(II).

We are still not certain how to assign the transition but suspect if arises from the lone pair on the oxygen (this being absent when  $-O^-$  is replaced by  $-NH^-$ )

21. R. H. Holm and F. A. Cotton, J. Am. chem. Soc. 80, 5658 (1958).

22. P. E. Wright, M. Sc. thesis, University of Auckland (1969).

<sup>20.</sup> P. E. Wright, Private communication.

and propose therefore an  $n \to \pi^*$  transition, this  $\pi^*$  orbital being largely, although not entirely, unaffected by substituents on the benzene ring. Final assignment must await detailed investigations of band shifts under molecular changes (where these can be measured for an absorption shoulder), single crystal studies, or energy level calculations.