Inorganica Chimica Acta, 102 (1985) 121–125

Divalent Metal Complexes of the Schiff's Base N,N-(2-hydroxy-5-methyl-1,3-dibenzylidine)-bis-(4-methyl-2-sulphonic acid aniline)

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Received October 23, 1984

Abstract

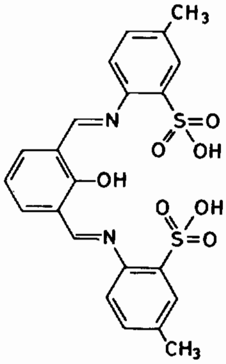
The Schiff's base, N,N-(2-hydroxy-5-methyl-1,3-dibenzylidine)-bis-(4-methyl-2-sulphonic acid aniline) (≡alsapH_3), derived from 4-methyl 2-sulphonic acid aniline (2 mol) and 2-hydroxy 5-methyl isophthalaldehyde forms highly coloured complexes with a range of divalent metal ions. On the basis of their colours the complexes fall into two groups. Those of Mg^{2+}, Mn^{2+} and Fe^{2+} have their principal diffuse reflectance band at 536 nm and are deep red while those of Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} have a band between 462 and 486 nm and are yellow-red. It is suggested that the two groups have different solid state structures and that these are dependent on the electronegativity of the metal ion. Some possible structures are discussed in the light of the electronic and infra-red spectra of the complexes. Ni^{2+} and Zn^{2+} complexes of the homologous Schiff's base derived from 2-hydroxy 5-methyl isophthalaldehyde and 2-amino 1-naphthalene sulphonic acid (≡alsatH_3) have also been prepared.

Introduction

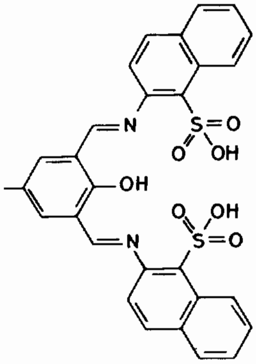
We have previously reported a series of metal complexes of an aromatic Schiff's base in which the metal ions are thought to play an important part in influencing the tautomeric form adopted by the coordinated ligands [1]. These complexes were of interest in that they offered the possibility of a more general approach to the synthesis of metal-containing pigments by extending the range of usable metal ions.

It was of interest to develop the idea of generality of structure in Schiff's base metal complexes and we now report the preparation of a new series derived from 2-hydroxy 5-methyl isophthalaldehyde and an *ortho* sulphonic acid substituted aromatic amine.

The new complexes are derivatives of the potentially tri-ionic ligand alsap H_3 which was not itself isolated. The structure of this ligand is such that direct contact along the plane of the molecule between a metal ion and either an azomethine or the hydroxy group is impossible with a considerable distortion from planarity. It was hoped, therefore, that a divalent metal ion might leave these groups intact and instead coordinate to the two sulphonate groups whose distance apart within the ligand molecule would seem to facilitate this. The metal would then be independent of the principal 'organic' chromophore and this would be of interest with respect to the development of more generalised metal-containing pigment systems.



alsap H_3



alsat H_3

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Complexes of alsap H_3 with the divalent ions Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} have been prepared and their solid state electronic and infra-red spectra recorded. Some possible solid state structures are discussed in the light of these spectra. Ni^{2+} and Zn^{2+} complexes of the homologous ligand alsat H_3, derived from 2- amino 1-naphthalene sulphonic acid, have also been prepared.

Results and Discussions

The complexes of alsapH_3 with divalent metal ions were found to fall into two distinct groups on the basis of their colours. The first group comprises complexes of the ions Mg^{2+}, Mn^{2+} and Fe^{2+}, each of which is characterized by an intense band at 536 nm in its visible solid state diffuse reflectance spectrum (Table I). The complexes are bright red and are insoluble in water, acetone and chloroform but are slightly soluble in methanol. Analytical data (Table II) indicate that the manganese and iron complexes crystallise with two molecules of acetic acid or two acetate ions per metal atom, these presumably deriving from the metal acetate used in the preparations. A shortage of the dialdehyde starting material prevented measurement of the magnetic moment of the iron complex. However, when the complex was prepared under an atmosphere of nitrogen and the solid subsequently exposed to air for one week there was no change in the infra-red spectrum from that of the freshly isolated sample. This fact and the general appearance of the iron derivative suggests that it is an analogue of the magnesium and manganese complexes and that iron is therefore in the +II oxidation state. However, the possibility of oxygen-bridged iron(III) dimers cannot be ruled out on present evidence.

The deep colours of the red complexes are difficult to explain on the basis of established colour/structure correlations in azomethine systems [2]. One possible explanation is that the colour is associated with an intermolecular interaction, possibly involving hydrogen-bonding. This would be consistent with the low solubility of the complexes in polar solvents and also with the fact that the 536 nm band in the diffuse reflectance spectrum of the magnesium complex (alsapH)Mg·$4^1/_2H_2O$ is not present in the spectrum in methanol solution (10^{-3} M). Instead a band occurs at 466 nm ($\epsilon = 1.86 \times 10^3$ l cm^{-1} mol^{-1}) which is close to those found in the visible spectra of the second group of complexes (see later). The infra-red spectra of the Mg^{2+}, Mn^{2+} and Fe^{2+} complexes reveal no

TABLE I. Principal Band(s) in the Visible Region of the Diffuse Reflectance Spectra (nm) and Some Infra-Red Data (cm^{-1}) for the Prepared Compounds.

Compound	Solid state diffuse reflectance band		ν(C=N) (Nujol mull spectra)
(alsapH)Mg·$4^1/_2H_2O$	536		1636
(alsapH)Mn·$1^1/_2H_2O$·2HOAc	536		1635
(alsapH)Fe·$1^1/_2H_2O$·2HOAc	478	536	1639
(alsapH)Co·$4^1/_2H_2O$	476		1628
(alsapH)Ni·$4^1/_2H_2O$	486		1630
(alsapH)Cu·$4H_2O$	466		1636
(alsapH)Zn·$4^1/_2H_2O$	464		1634
(alsatH)Ni·$3H_2O$	500		1630
(alsatH)Zn·$3H_2O$	474		1637

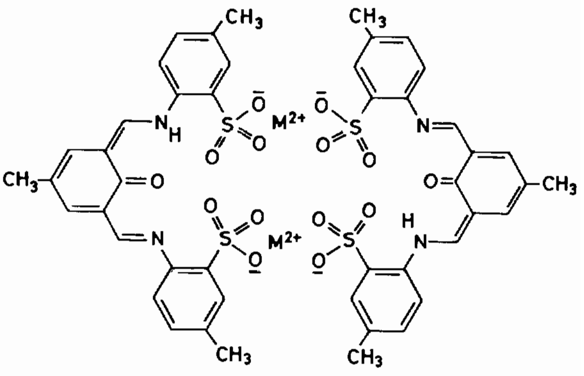
TABLE II. Elemental Analyses of the Compounds Prepared.

Compound	Carbon %		Hydrogen %		Nitrogen %	
	Calc.	Found	Calc.	Found	Calc.	Found
(alsapH)Mg·$4^1/_2H_2O$	45.47	45.45	4.78	4.85	4.61	4.53
(alsapH)Mn·$1^1/_2H_2O$·2HOAc	46.15	46.31	4.42	4.38	3.99	4.12
(alsapH)Fe·$1^1/_2H_2O$·2HOAc	46.09	46.23	4.41	4.63	3.98	3.66
(alsapH)Co·$4^1/_2H_2O$	43.13	43.24	4.53	4.25	4.38	3.88
(alsapH)Ni·$4^1/_2H_2O$	43.13	43.03	4.53	4.35	4.38	4.21
(alsapH)Cu·$4H_2O$	43.39	43.27	4.40	4.35	4.40	4.32
(alsapH)Zn·$4^1/_2H_2O$	42.59	42.63	4.47	4.46	4.32	4.40
(alsatH)Ni·$3H_2O$	50.65	50.69	3.78	3.74	4.08	4.17
(alsatH)Zn·$3H_2O$	50.29	50.27	3.76	3.93	4.05	4.05

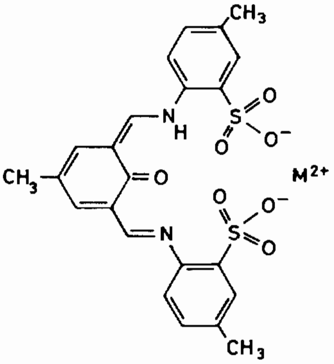
unusual features which might provide an understanding of the structure of the complexes although there is no band at *ca.* 1700 cm^{-1} attributal to acetic acid. A band at *ca.* 1637 cm^{-1} is attributed to ν(C=N) and a broad band centred on *ca.* 1200 cm^{-1} is probably due to vibrations of the $-SO_3^-$ group [3]. It is likely, for reasons previously discussed, that the metal ions are associated with the sulphonate groups. The constancy of the position of the 536 nm band in the diffuse reflectance spectra of all these red complexes suggests that in each case the metal ion has no influence on the chromophore once it is established. However, the nature of the metal ion is clearly important in forming the chromophore in the first place and in this respect it is the lower (Allred-Rochow) electronegativities [4] of Mg(II), Mn(II) and Fe(II) which appear to distinguish them from the other metals used in this study. The possible implications of this for the structures of these 'red' complexes are discussed later.

The second group of complexes comprises those of the ions Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}. These are characterised by the occurrence of a band between 464 nm and 486 nm (Table I) in their solid state diffuse reflectance spectra which renders the complexes deep yellow to red-yellow in colour. Of particular significance is the fact that this principal absorption band varies in position from complex to complex suggesting that, in contrast to the 'red' group, the metal ion in this series has an important influence on the solid state chromophore. It is unlikely, for steric reasons, that the metal ion is coordinated to an azomethine nitrogen atom but it is possible that the ion has an indirect effect on this 'organic' chromophore via its role in the structure of the complex. The zinc derivative (alsapH)Zn$\cdot 4^1/_2 H_2O$ has its principal visible band at 464 nm in the solid state diffuse reflectance spectrum while in methanol solution the band is at 462 nm (428 sh). This suggests that the solid state and dissolved species have similar structures in the case of this complex and that the solid state colour, again in contrast to the situation in the 'red' series, is not likely to be derived from an inter-molecular interaction. In fact the position of the visible bands in the spectra of the zinc complex is consistent with a β-keto amine form for the coordinated ligand [5], although this cannot be established with certainty.

On the basis of present evidence we suggest that the solid structures of the complexes in the 'red' and 'yellow' series are as depicted in the diagrams I and II. The exact natures of the chromophores in the two series and the possible structural role of acetate in the Mn, Fe complexes are not known but the positions of the metal ions as shown in the diagrams are consistent with the spectral data (Table I). While there are differences between the infra-red spectra (chiefly in the regions associated with $-SO_3^-$ vibrations) of the two series, the position of the band assigned to ν(C=N) does not greatly vary.



I 'Red Series', M = Mg, Mn, Fe



II 'Yellow' Series, M = Co, Ni, Cu, Zn

The influence of the metal on the chromophore will be more important in the 'yellow' series (II) where the ionic radius and the electronegativity of the metal ion can be expected to dictate the distance between sulphonate, and hence azomethine, groups within the molecule. The variation in the position of the solid state diffuse reflectance band among complexes in this series can then be understood. In the proposed dimeric structure of the 'red' complexes, however, the metal ion can be expected to have no significant influence on the distance between azomethine groups in the same molecule. Consequently the visible reflectance band in the spectra of complexes in this series is at 536 nm in all the examples.

It is interesting to note that the reflectance spectrum of the 'red' iron complex contains an intense band at 478 nm, in the visible region, in addition to that at 536 nm. The shorter wavelength band is in the region associated with reflectance bands of the 'yellow' series and may indicate that the iron complex exists in both forms in the solid state. This possible 'borderline' nature of iron in respect of the two proposed structures might provide a clue as to the distinction between metals that forms 'yellow' complexes and those that form 'red' complexes. It has already been suggested that the lower Allred-Rochow electronegativities of Mg(II), Mn(II) and Fe(II) may lead to these metals forming complexes of a different structure from those of Co(II), Ni(II), Cu(II) and Zn(II). This argument is strengthened by the observation that the A-R electronegativity of the 'borderline' Fe(II) (1.64) is between those of Mn(II) (1.60), which forms a 'red' complex, and Zn(II) (1.66), which forms a 'yellow' complex. It is suggested therefore that as the electronegativities of the metals decrease so do the stability constants of their 'yellow' complexes. (There seems incidentally to be a further correlation between the electronegativities and the positions of the principal visible reflectance bands for Co(II), Ni(II) and Zn(II)). At a particular electronegativity value the metal ion is no longer able to 'pull' the sulphonate groups together to form a 'yellow' complex(II). Metals with electronegativities below this critical value therefore form 'red' complexes(I).

The infra-red and solid state diffuse reflectance spectra of the Ni(II) and Zn(II) complexes of the ligand alsatH_3, which have also been prepared, indicate that these complexes have structures similar to 'yellow' derivatives of alsapH_3.

Experimental

Physical Measurements

Infra-red spectra were recorded on a Perkin-Elmer 457 instrument and calibrated with polystyrene. Electronic spectra in solution and in the solid state (diffuse reflectance) were recorded on a Pye-Unicam SP1800 instrument.

Preparations

(alsapH)Mg·4½H_2O, (alsapH)Mn·1½H_2O·2HOAc, (alsapH)Fe·1½H_2O·2HOAc

These three complexes—which constitute the 'red' group—were prepared by the same method using the appropriate metal acetate or, in the case of iron, ferrous sulphate and sodium acetate. The method is illustrated by the preparation of the manganese complex.

Manganese(II) acetate (0.245 g, 0.001 mol) and 4-methyl 2-sulphonic acid aniline (0.374 g, 0.002 mol) were dissolved in hot water (15 cm^3). The solution was filtered and then stirred at 60° on a hotplate. To this stirred solution was added, dropwise, a solution of 2-hydroxy 5-methyl isophthaldehyde (0.164 g, 0.001 mol) in boiling water (75 cm^3). The red solution was allowed to cool and was then filtered again. On standing overnight at 5° the solution deposited red crystals of the complex. These were filtered off, washed with water and then with acetone until the washings were colourless (or pale pink) and dried over silica gel under vacuum.

In the preparation of the iron(II) complex the solutions at each state were flushed with nitrogen. All three complexes gave samples of analytical purity in the aforementioned preparation but could be recrystallised from boiling water. A recrystallised sample of the manganese(II) complex gave analysis figures identical to that of a sample isolated from the above preparation. Yields from preparations: Mg = 62%, Mn = 53%, Fe ≃ 30%.

(alsapH)M·4½H_2O (M = Co, Ni, Zn)

These three complexes were prepared by the same method using the appropriate metal acetate. The method is illustrated by the preparation of (alsapH)-Zn·4½H_2O.

Zinc(II) acetate (0.220 g, 0.001 mol) and 4-methyl 2-sulphonic acid aniline (0.374 g, 0.002 mol) were dissolved together in water (25 cm^3). The solution was filtered and stirred using a magnetic stirrer. A solution of 2-hydroxy 5-methyl isophthalaldehyde (0.164 g, 0.001 mol) in ethanol (25 cm^3) was added dropwise at room temperature (22°). Stirring was continued for a further 2 h and then the orange solid was filtered off, washed with water and dried over silica gel under vacuum.

It was necessary to recrystallise the nickel(II) complex from water in order to obtain an analytical pure sample. The other two metals gave pure samples directly from the above preparation. Yields: Zn = 71%, Co and Ni ≃ 50%.

(alsapH)Cu·4H_2O

4-methyl 2-sulphonic acid aniline (0.187 g, 0.001 mol) dissolved in boiling water (25 cm^3) was mixed with a solution of 2-hydroxy 5-methyl isophthalaldehyde (0.082 g, 0.0005 mol) in hot ethanol (5 cm^3). The solution was filtered hot and then cooled to room temperature. The now red solution was stirred with a magnetic stirrer and to it was added, dropwise, a solution of copper(II) acetate (0.1 g, 0.0005 mol) in water (10 cm^3). The yellow solid was filtered off, washed with water and dried over silica gel under vacuum. Yield = 68%.

(alsatH)M·3H_2O (M = Ni, Zn)

The complexes were prepared by the same method which is illustrated by the preparation of the nickel derivative.

Nickel(II) acetate (0.125 g, 0.0005 mol) and 2-amino 1-naphthalene sulphonic acid (0.223 g, 0.001 mol) were dissolved together in water (12 cm^3). The solution was filtered and stirred using a magnetic stirrer. 2-hydroxy 5-methyl isophthalaldehyde (0.082 g, 0.0005 mol) dissolved in ethanol (6 cm^3) was then added to this stirred solution dropwise at room temperature. Stirring was continued for a further 2 h and then the red solid was filtered off, washed with water and ethanol and dried under silica gel under vacuum. Yield = 74%. Yield of zinc complex = 79%.

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