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The Crystal Structure of the Copper–Magnesium Complex with the Binucleating Schiff Base of Ethylenediamine with 3-Formylsalycylic Acid

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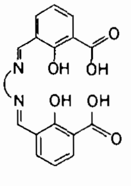
The X-ray structure determination of [CuMg(fsaen)]3H_2O is reported. The ligand fsaen^{4-}, in this complex, is the anion of the Schiff base of ethylenediamine with 3-formylsalycylic acid. This binucleating ligand provides a planar N_2O_2 donor grouping for the copper(II) ion and a planar O_4 donor grouping for the magnesium(II) ion. Two axial water molecules complete octahedral coordination to the magnesium ion. The ligand has a slightly stepped conformation. The electronic spectrum of the copper(II) ion is compared to the spectra of copper(II) ions in other complexes of fsaen^{4-}, and the relationships between such spectra and the structures of the complexes are discussed.

Introduction

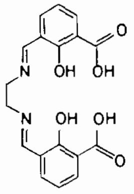
Many complexes of binucleating ligands have been investigated in recent years [1–13]. Most such ligands have equivalent donor sites and yield homobinuclear complexes which contain two similar metal ions [1–5]. Binucleating ligands with dissimilar donor sites have been less well studied [5–13]. The stepwise addition of two different metal ions, to coordinatively selective ligands of this type, can produce heterobinuclear complexes which contain two different metal ions [6, 7, 9–12].

The reaction of 3-formylsalycylic acid with diamines yields binucleating Schiff bases (referred to as H_4fsada ligands) which have N_2O_2 and O_4 coordination sites (see I) [6–11]. These H_4fsada ligands can produce heterobinuclear complexes which contain either one transition metal ion and one non-transition metal ion, or two transition metal ions [6, 7, 9–11]. We shall use the formalism [MM'(fsada)] to indicate a complex in which the metal ions M and M' are located in the N_2O_2 and O_4 sites, respectively, of an fsada^{4-} ligand. When M is in the N_2O_2 site, but the location of M' is uncertain, we use the formalism MM'(fsada).



(I) Binucleating H_4fsada ligands.

The spectra and modes of preparation of [MM'(fsada)] complexes have been used as indications of their structures [6, 7, 9, 10] and the spectrum of the copper(II) ion in the N_2O_2 site has been correlated with the bonding situation at the O_4 site [6, 9]. In order to test these relationships, we have carried out an X-ray structure analysis on [CuMg(fsaen)]3H_2O, a copper-magnesium complex with the Schiff base H_4fsaen (II) of ethylenediamine with 3-formylsalycylic acid. This is the first report of a structure analysis on a binucleated complex of a derivative of 3-formylsalycylic acid. Some spectroscopic data on related complexes are also reported.



(II) The Schiff base H_4fsaen.

Experimental

[CuMg(fsaen)]3H_2O

A warm aqueous solution (150 ml) of $MgSO_4 \cdot 7H_2O$ (0.25 g) was added with stirring to a warm aqueous solution (150 ml) of $CuNa_2$(fsaen)3H_2O [14] (0.5 g), yielding a pink flocculent precipitate which later became brick-red and granular. The mixture was digested on the steam bath for 3 days and a portion of the brick-red precipitate, after being filtered off, analysed as [CuMg(fsaen)]3H_2O. *Anal.* Calcd. for $C_{18}H_{12}N_2O_6CuMg \cdot 3H_2O$: C, 44.1; H, 3.9;

N, 5.9; Cu, 12.6; Mg, 4.9. Found: C, 43.7; H, 3.7; N, 5.7; Cu, 12.9; Mg, 4.9%.

The mixture was digested for several weeks on the steam bath with periodic addition of water, during which time ruby-red crystals appeared. *Anal.* Calcd. for $C_{18}H_{12}N_2O_6CuMg\cdot 3H_2O$: C, 44.1; H, 3.9; N, 5.9; Found C, 43.8; H, 3.5; N, 5.7%.

Cu(H₂fsaen)

A mixture of 1.0 *M* acetic acid (3 ml) and water (50 ml) was added with stirring to an aqueous solution (150 ml) of $CuNa_2(fsaen)3H_2O$ [14] (0.5 g). The violet complex immediately precipitated, was filtered off, washed with water, and dried under vacuum. *Anal.* Calcd. for $C_{18}H_{14}N_2O_6Cu$: C, 51.7; H, 3.4; N, 6.7; Cu 15.2. Found: C, 51.5; H, 3.3; N, 6.2; Cu, 15.4%.

CuBa(fsaen)2H₂O

An aqueous solution (150 ml) of barium chloride dihydrate (0.24 g) was added slowly with stirring to a warm aqueous solution (150 ml) of $CuNa_2(fsaen)$-$3H_2O$ [14] (0.5 g). The resulting suspension was digested on a steam bath for 3 hr and the blue-grey precipitate was then filtered off, washed with water and dried in a vacuum desiccator. The compound effloresced to a voluminous blue-grey powder after 2 days in the desiccator. *Anal.* Calcd. for $C_{18}H_{12}N_2O_6CuBa\cdot 2H_2O$: C, 36.5; H, 3.0; N, 5.0; Cu, 10.9; Ba, 23.3. Found: C, 36.7; H, 2.7; N, 4.7; Cu, 10.8; Ba, 23.3%.

Analyses and Physical Measurements

These were as previously described [6].

Collection and Reduction of X-ray Data

The crystal and molecular structure of $C_{18}H_{12}N_2O_6CuMg\cdot 3H_2O$ has been determined using X-ray diffraction methods. The compound crystallises in space group $P3_121$ or $P3_221$. It was not possible to differentiate between either of these space groups as the breakdown in Friedel's law was not conclusive [15–17].

The unit cell dimensions and intensity data were collected on a Siemens automatic single crystal diffractometer. The unit cell dimensions were determined as $a = b = 12.84 \pm 0.05$ Å; $c = 9.99 \pm 0.05$ Å; $\alpha = \beta = 90°$; $\gamma = 120.0°$.

The intensity data were recorded using CuKα radiation [$K\alpha_1 = 1.54051$, $K\alpha_2 = 1.54433$ Å] and nickel attenuators. A total of 1067 independent reflections were recorded and corrected for Lorentz, polarisation and absorption ($\mu = 23.4$ cm^{-1}) effects [18].

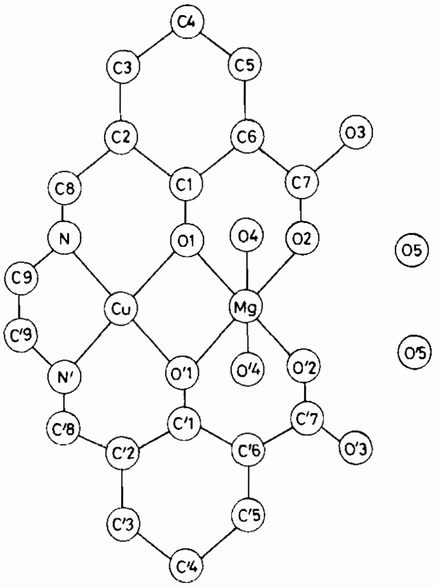


Figure 1. The atom numbering scheme for $[CuMg(fsaen)]\cdot 3H_2O$.

Solution and Refinement of the Structure

There are three molecules of complex per unit cell, necessitating the Cu and Mg atoms to be located on special positions of two-fold symmetry. The structure was elucidated using heavy atom and Patterson methods [19]. The Cu and Mg atoms were located from a Patterson synthesis on the basis of space group $P3_121$.

The final structure was refined by full matrix least-squares methods. The final anisotropic refinement converged to a reliability index of 0.040 for a structure in which the hydrogen atoms associated with the complex (excluding those associated with the water molecules) were idealised and assigned temperature factors equal to those of the atoms to which they are bonded.

There are three molecules of water associated with each molecule of complex. Two symmetry related molecules of water are bonded in the octahedral sites of the magnesium atom. The third molecule of water is trapped within the crystal lattice. However, as this molecule is very close to the two-fold axis of symmetry passing through the Cu and Mg atoms, the distance between the oxygen and a symmetry related atom is 1.965(6) Å. This distance is uncomfortably close, considering the closest hydrogen bond approach distances reported are *ca.* 2.4 Å [20].

The thermal parameters for this oxygen atom were, at this stage, observed to be unusually high. In addition, the chemical analysis indicated only three molecules of water, whereas a complete atom implied four molecules of water per molecule of complex. All these factors led to the final proposed structure

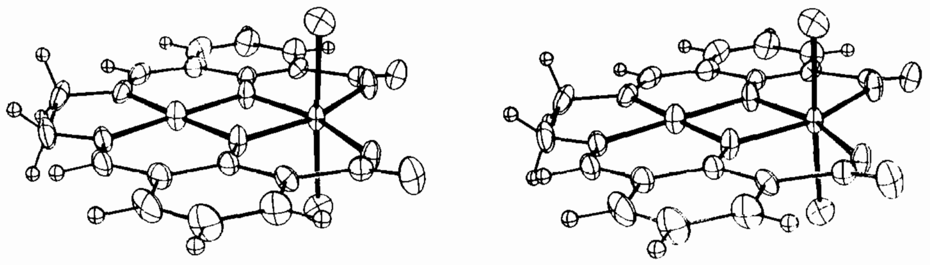


Figure 2. Stereoscopic view of [CuMg(fsaen)] $3H_2O$.

TABLE I. Final Atomic Coordinates and Anisotropic Thermal Parameters[a] with Standard Deviations.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.5506(1)	0.0000(0)	0.3333(0)	0.0038(1)	0.0056(1)	0.0081(1)	0.0028(0)	0.0001(0)	0.0002(1)
Mg	0.7843(2)	0.0000(0)	0.3333(0)	0.0020(1)	0.0015(2)	0.0063(3)	0.0008(0)	0.0003(0)	0.0006(2)
O(1)	0.7191(3)	0.1166(4)	0.3382(4)	0.0025(3)	0.0028(3)	0.0091(4)	0.0015(2)	−0.0003(3)	−0.0002(3)
O(2)	0.9444(3)	0.1452(4)	0.3544(4)	0.0027(3)	0.0027(3)	0.0090(4)	0.0014(3)	−0.0000(3)	0.0006(3)
O(3)	1.0909(4)	0.3288(4)	0.3098(5)	0.0032(3)	0.0029(3)	0.0105(5)	0.0009(3)	0.0013(3)	0.0001(3)
O(4)	0.7960(4)	0.0133(4)	0.1222(4)	0.0061(3)	0.0042(3)	0.0064(4)	0.0022(3)	0.0012(3)	0.0010(3)
O(5)	0.0490(8)	−0.0463(7)	0.2495(8)	0.0057(7)	0.0062(6)	0.0104(7)	0.0026(6)	0.0015(6)	0.0017(5)
N	0.5002(5)	0.1174(5)	0.3408(5)	0.0048(4)	0.0064(5)	0.0047(4)	0.0042(4)	0.0008(3)	0.0007(3)
C(1)	0.7706(6)	0.2326(6)	0.3358(5)	0.0040(6)	0.0040(5)	0.0043(5)	0.0027(5)	−0.0000(4)	−0.0001(4)
C(2)	0.7017(6)	0.2925(6)	0.3369(5)	0.0060(5)	0.0049(5)	0.0049(5)	0.0041(5)	−0.0002(4)	−0.0000(4)
C(3)	0.7612(7)	0.4195(6)	0.3362(6)	0.0083(7)	0.0043(5)	0.0078(6)	0.0049(5)	0.0009(5)	0.0004(4)
C(4)	0.8842(6)	0.4876(6)	0.3314(8)	0.0072(6)	0.0031(5)	0.0105(7)	0.0031(4)	0.0004(5)	−0.0005(5)
C(5)	0.9502(6)	0.4306(5)	0.3287(6)	0.0052(5)	0.0027(4)	0.0089(6)	0.0017(4)	−0.0000(5)	−0.0005(4)
C(6)	0.8982(5)	0.3042(5)	0.3313(5)	0.0044(5)	0.0025(4)	0.0052(5)	0.0022(4)	0.0005(4)	−0.0002(3)
C(7)	0.9831(5)	0.2556(5)	0.3305(5)	0.0034(4)	0.0028(4)	0.0048(5)	0.0014(4)	−0.0001(3)	−0.0003(3)
C(8)	0.5740(7)	0.2329(8)	0.3402(6)	0.0070(6)	0.0071(6)	0.0048(5)	0.0058(5)	0.0002(5)	0.0001(4)
C(9)	0.3691(6)	0.0672(7)	0.3499(7)	0.0054(6)	0.0088(7)	0.0073(6)	0.0056(5)	0.0023(5)	0.0023(5)
HC(3)	0.7119(0)	0.4600(0)	0.3383(0)						
HC(4)	0.9229(0)	0.5758(0)	0.3301(0)						
HC(5)	1.0403(0)	0.4805(0)	0.3226(0)						
HC(8)	0.5310(0)	0.2793(0)	0.3420(0)						
HC(91)	0.3442(0)	0.1078(0)	0.2820(0)						
HC(92)	0.3467(0)	0.0788(0)	0.4403(0)						

[a] Each hydrogen atom is assigned the same thermal parameters as those for the atom to which the hydrogen atom is bonded.

which contains three molecules of water per molecule of complex and assumes fifty percent occupancy for the third water molecule. The refinement of this revised structure resulted in a decrease in the reliability index from 0.054 to 0.040. A listing of the observed and calculated structure factors is available from the authors (J.P.B. or D.J.P).

Description of Structure

The molecular structure is shown in Figures 1 and 2, and structural data are given in Tables I–IV. The fsaen^{4-} molecule is almost planar, and has a copper(II) ion located in its N_2O_2 site, and a magnesium ion in its O_4 site. A two-fold axis passes through the metal ions. The coordination about the copper(II) ion is almost exactly planar; the N_2O_2 donor atoms deviate by ±0.01 Å, in a tetrahedral distortion, from their least squares plane (Table IV). The closest intermolecular approach to the copper(II) ion is from copper(II) ions in symmetry related molecules in adjacent unit cells parallel to the *c*-axis direction. The Cu–Cu distance is 9.987 Å. The magnesium ion is coordinated in a regular octahedral arrangement by two axially disposed water molecules and by four oxygen atoms from the ligand.

The ligand molecule is almost planar and has a slightly stepped conformation, in the terminology used for the related Schiff bases of salicyaldehydes with diamines [21]. The angle (ϕ) between the donor atom plane N,N′, O(1), O′(1) and either NCCCO chelate plane (*e.g.* N, C(8), C(2), C(1), O(1)) is 3.5°. The half-step distance (σ) from the copper(II) ion

TABLE II. Interatomic Distances[a] with Standard Deviations (Å).

Cu–N	1.917(3)	C(4)–C(5)	1.371(3)
Cu–O(1)	1.920(3)	C(5)–C(6)	1.412(3)
Mg–O(1)	2.049(3)	C(6)–C(1)	1.423(3)
Mg–O(2)	1.978(2)	C(6)–C(7)	1.503(3)
Mg–O(4)	2.115(3)	C(7)–O(3)	1.242(3)
N–C(8)	1.301(3)	C(7)–O(2)	1.269(3)
N–C(9)	1.474(3)	C(9)–C′(9)	1.530(6)
O(1)–C(1)	1.293(3)	Cu–Mg	3.001(4)
C(1)–C(2)	1.433(3)	Cu–O(4)	3.723(4)
C(8)–C(2)	1.422(4)	Mg–O″(5)	3.861(4)
C(2)–C(3)	1.414(3)	O(5)–O′(5)	1.965(6)
C(3)–C(4)	1.370(4)		

[a]The symbol C′ refers to the atom C at x – y, ȳ, 2/3 – z. The symbol C″ refers to the atom C at 1 – y, x – y, 1/3 + z.

TABLE IV. Deviation[a] of Atoms from Least Squares Plane through N,N′, O(1), O′(1).

Deviations[a] (Å)					
N	0.0128	O(1)	–0.0129		
N′	–0.0128	O′(1)	0.0129		
Cu	0.0000	C(1)	–0.0988	C(6)	–0.1813
Mg	0.0000	C(2)	–0.1189	C(7)	–0.1637
O(2)	0.1334	C(3)	–0.1935	C(8)	–0.0553
O(3)	–0.4090	C(4)	–0.2774	(C(9)	0.1294
O(5)	–0.8116	C(5)	–0.2736		

[a]The deviations of O′(n) and C′(n) atoms are equal and opposite to the deviations of the corresponding O(n) and C(n) atoms.

to either NCCCO chelate plane is 0.08 Å in keeping with the slightly stepped conformation,, the distances from the ethylene carbon atoms, C(9) and C′(9), to the N_2O_2 donor plane are ±0.13 Å, and the N, C(9), C′(9), N′ dihedral angle is 17.4°. In a perfectly regular planar conformation all of the above quantities would be zero [21].

Discussion

The methods of preparation and electronic spectra of [MM′(fsada)] complexes have been used as indications of their structures [6, 7, 9, 10]. Work up to now suggests that the N_2O_2 site is preferentially occupied by a copper(II) ion or a nickel(II) ion reacting with an H_4fsada molecule, so that only the O_4 site is available for any subsequent metal ion [6, 7, 9–11]. Copper(II) ions bonded to fsada^{4-} molecules (based on ethylenediamine, 1,2-diaminopropane, 1,3-diaminopropane, *o*-phenylenediamine and 1,2-cyclohexanediamine) have an electronic absorption band at either *ca.* 12,000–15,000 cm^{-1} or *ca.* 17,500–20,000 cm^{-1}, and it has been assumed that these ranges correspond to copper(II) situated in either the O_4 or N_2O_2 coordination sites, respectively [6–10]. The complex [CuMg(fsaen)]$3H_2O$ has a reflectance band at 19,500 cm^{-1} (Figure 3) and it was made by reacting copper(II), then magnesium(II), with the ligand. These factors would suggest that the copper(II) ion is in the N_2O_2 site. The structure determination shows that this is the case, and so the structure provides the first crystallographic backing for the assumptions discussed above for H_4fsada systems. The magnetic and spectroscopic properties of complexes of the type [CuM(fsada)]nH_2O (M = Ni, Co) have been interpreted in terms of structures similar to that of [CuMg(fsaen)]$3H_2O$, *i.e.* structures in

TABLE III. Bond Angles and Their Standard Deviations (°).

N–Cu–N′	86.0(1)	N–C(9)–C′(9)	110.9(1)
N–Cu–O(1)	94.5(1)	O(1)–C(1)–C(2)	121.4(2)
N–Cu–O′(1)	179.1(1)	O(1)–C(1)–C(6)	120.4(2)
O(1)–Cu–O′(1)	85.0(1)	O(2)–C(7)–O(3)	122.9(2)
Cu–N–C(8)	123.8(2)	O(2)–C(7)–C(6)	120.2(2)
Cu–N–C(9)	114.8(2)	O(3)–C(7)–C(6)	116.9(2)
Cu–O(1)–Mg	98.2(1)	C(1)–C(2)–C(3)	119.7(2)
Cu–O(1)–C(1)	128.7(1)	C(1)–C(2)–C(8)	124.6(2)
O(1)–Mg–O′(1)	78.2(1)	C(1)–C(6)–C(5)	118.3(2)
O(1)–Mg–O(2)	85.4(1)	C(1)–C(6)–C(7)	124.9(2)
O(1)–Mg–O′(2)	163.4(1)	C(2)–C(1)–C(6)	118.3(2)
O(2)–Mg–O′(2)	110.8(1)	C(2)–C(3)–C(4)	121.5(2)
Mg–O(1)–C(1)	132.9(2)	C(3)–C(2)–C(8)	115.6(2)
Mg–O(2)–C(7)	132.5(1)	C(3)–C(4)–C(5)	118.9(2)
C(8)–N–C(9)	121.4(2)	C(4)–C(5)–C(6)	123.4(2)
N–C(8)–C(2)	126.8(2)	C(5)–C(6)–C(7)	116.9(2)

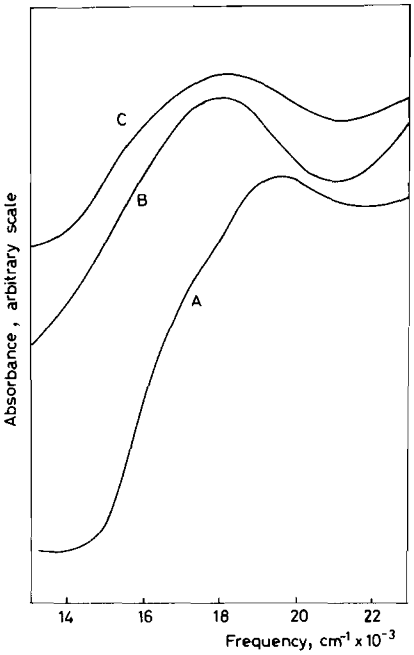


Figure 3. Diffuse reflectance spectra: (A), [CuMg(fsaen)]-$3H_2O$; (B), CuBa(fsaen)$2H_2O$; (C), Cu(H_2fsaen).

which the metal ion M is six-coordinate, with water molecules coordinated in the axial positions [9, 10].

The electronic spectrum of a copper(II) ion in the N_2O_2 site of some H_4fsada ligands (based on ethylenediamine, 1,2-diaminopropane and 1,2-diamino-2-methylpropane) may be used as an indication of the coordination occurring at the O_4 site, provided the copper(II) band is well clear of any absorption from the second metal ion [6, 22]. When no metal occupies the O_4 site, the copper(II) ion absorbs at *ca.* 17,500–18,500 cm^{-1}, for example Cu(H_2fsaen) has a band at 18,100 cm^{-1} (see Figure 3) [6, 22]. In contrast, an absorption at *ca.* 19,000–20,000 cm^{-1}, produced by a copper(II) ion in a N_2O_2 site, seems to indicate that an accompanying metal ion is in the adjacent, undistorted O_4 site [6, 22]. Copper(II) band frequencies of *ca.* 18,000 cm^{-1} appear to occur for some [CuM(fsada)] complexes, but only when the copper(II) band is superimposed on some absorption from the second metal ion, so that the absorption frequency is not accurately discernible [8, 10]. The structure determination supports this correlation since the complex [CuMg-(fsaen)]$3H_2O$ absorbs at 19,500 cm^{-1} (Figure 3) and the O_4 site is shown to be occupied by the magnesium ion. As an explanation of this correlation, it was suggested that a metal ion in the O_4 site would enhance the planarity of the coordination about a copper(II) ion in the N_2O_2 site, leading to the observed higher absorption frequency for the copper(II) ion [6, 9]. The structure of [CuMg-(fsaen)]$3H_2O$ is consistent with this explanation, since the N_2O_2 arrangement about the copper(II) ion is almost exactly planar.

With species of the type [CuM(fsaen)], a large M metal ion would not be expected to fit into an undistorted O_4 site. With the group IIA ions, this effect is noticeable with barium, since CuBa(fsaen)$2H_2O$ is blue-grey and has a reflectance band at 18,000 cm^{-1} (Figure 3), whereas the complexes [CuM^{II}(fsaen)]·nH_2O (with M as Mg, Ca, or Sr) [22] are brick-red and have a band in the range 19,000 to 19,500 cm^{-1}. We reported a similar result with the corresponding complexes based upon 1,2-diaminopropane [6].

The low absorption frequency in the copper–barium compound could occur because the barium ion is too large for the O_4 site, and the complex is not binucleated. Alternatively, the barium ion might be located in, or above, the O_4 site, causing ligand distortion. This distortion could involve longer Cu–N and Cu–O bonds, or less planar coordination to the copper(II) ion, and both effects would lower the absorption frequency of the copper(II) ion.

In the discussion above we have correlated the absorption spectrum of a copper(II) ion in the N_2O_2 site with the bonding situation at the O_4 site, and we have assumed four-coordination for the copper(II) ion. If the coordination number of the copper(II) increased to five or six, this would also influence the absorption spectrum. In every case, of which we are aware, the prediction about the geometry of the O_4 site, made on the basis of the spectrum of the copper(II) ion, correlates with factors such as the size of the second metal ion, or with its absence, and with conductivity and magnetic evidence. This close correlation, between the spectra of the copper(II) ion and the geometry of the O_4 site, makes it rather unlikely that the spectral changes are caused by fortuitous changes in the coordination number of the copper(II) ion.

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