*Inorganica Chimica Acta, 135* (1987) 1–4

# Preparation of Trinuclear Adducts from Quadridentate Schiff Base Copper(II) Complexes with Metal(II,III) Nitrate

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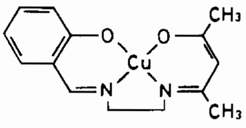
(Received May 2, 1986; revised July 23, 1986)

## Abstract

Trinuclear adducts of a quadridentate Schiff base copper(II) complex were prepared with metal(II,III) nitrate, where metal ions are Cu(II), Ni(II), Zn(II), Ca(II), Mg(II), Sr(II), Y(III), La(III) and Nd(III). They were characterized by means of elemental analyses, UV and IR spectra, as well as magnetic susceptibilities. Planarity of a copper environment in the Schiff base complex is enhanced in the order of a parent Schiff base complex, its binuclear adduct and the trinuclear. In a series of alkaline earth(II) and lanthanoid(III) adducts, two characteristic infrared bands arising from N=O frequencies of a nitrate group were observed around 1750 $cm^{-1}$, which demonstrates that the nitrate groups coordinate to the central metal(II,III) ions. The kinds of counter anions of the metal(II,III) salts are one of the important factors which control the adduct formations.

## Introduction

Quadridentate Schiff base metal(II,III) complexes are well-known to coordinate to inorganic and organic cations, resulting in polynuclear adducts [1, 2]. Studies of bi- and trinuclear copper(II) adducts have received considerable attention because their electronic spectra and magnetic properties are interesting, and they also provide models for metallo enzymes [3, 5]. Some binuclear adducts are of further interest because they have two metal centers with very different acid–base properties, with which a small molecule such as carbon dioxide can coordinate to the centers and be also activated [6, 7]. Sinn and his coworkers reported that (*N,N'*-disalicylidene-ethylenediaminato)copper(II), CuS forms the binuclear adduct with copper(II) chloride and, similarly, the trinuclear adduct with copper(II) perchlorate; detailed magnetic properties of the adducts were also studied [8–11]. Those structures have also been determined by X-ray diffraction analyses [12, 13]. In this paper, we report that the trinuclear adducts are also prepared by the reaction of the quadridentate Schiff base copper(II) complex and metal(II,III) nitrate. In Fig. 1, the quadridentate Schiff base copper(II) complex which is used in the present study is shown.



CuSA

Fig. 1. The unsymmetrical Schiff base copper(II) complex.

## Experimental

### *Syntheses*

CuS, [*N,N'*-bis(1-methyl-3-oxobutylidene)ethylenediaminato]copper(II);CuA, and [*N*-(1-methyl-3-oxobutylidene)-*N'*-salicylideneethylenediaminato]-copper(II);CuSA were prepared by a literature method [14]. The solvents used for the preparation were reagent grade and were used without further purification.

### *$CuSACuCl_2$*

Copper(II) chloride dihydrate (0.51 g, 3.0 mmol) was added to 100 ml of an acetone solution of CuSA (0.92 g, 3.0 mmol), and the mixture was stirred at room temperature for 1 h. The obtained dark reddish brown precipitates were then recrystallized from acetone.

### *$(CuSA)_2Cu(NO_3)_2$*

Copper(II) nitrate trihydrate (0.36 g, 1.5 mmol) was added to 100 ml of the acetone solution of CuSA (1.0 g, 3.0 mmol), which was stirred at room temperature for 30 min. The obtained dark purple precipitates were recrystallized from acetone. Lanthanum(III) and neodymium(III) adducts were prepared in a method similar to that described above. A nickel(II),

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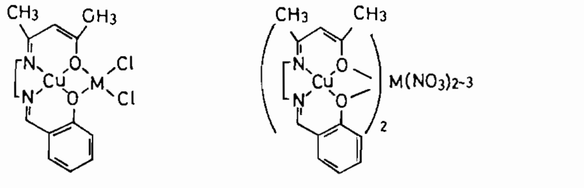
zinc(II) or strontium(II) adduct was prepared in a tetrahydrofuran (THF) solution, and was recrystallized from THF, acetone or methanol, respectively. Magnesium(II), calcium(II) and yttrium(III) adducts were prepared in the THF solutions, and were washed three times with THF.

*Measurements*

The electronic spectra in solution and the infrared spectra using nujol mulls were measured on a Hitachi 215 spectrophotometer and a Hitachi 124 spectrophotometer, respectively. The PA 115 Vibrating Sample Magnetometer, operated at 10 KG, was used to measure magnetic susceptibilities.

## Results and Discussion

The CuSA complex forms the binuclear adduct with copper(II) chloride dihydrate in the solution of acetone or THF and, similarly, the trinuclear adduct with copper(II) nitrate trihydrate (Fig. 2). The adducts were also directly obtained by the reaction of a free ligand with copper(II) chloride or nitrate. Although the bi- and trinuclear adducts of CuS as well as the trinuclear adduct of CuA were obtained, the reaction of CuA with copper(II) chloride formed an unknown adduct, the characterization of which could not be performed. In this study, the unsymmetrical quadridentate Schiff base copper(II) complex, CuSA, was mainly utilized due to the suitable solubilities of its bi- and trinuclear adducts. Elemental analyses, electronic and infrared spectra of d-block metal(II) (Ni, Cu and Zn) adducts are shown in Table I; similarly, those of alkaline earth(II) (Mg, Ca and Sr) and lanthanoid(III) (Y, La, and Nd) adducts are shown in Table II.



CuSAMCl2 (CuSA)2M(NO3)2-3

Fig. 2. The proposed models for the bi- and trinuclear adducts.

In the d-block metal(II) adducts, the formation of the bi- or trinuclear adducts was confirmed by elemental analyses and also by magnetic susceptibility dependences on temperature. In electronic spectra, the position of a d–d absorption band of the CuSA complex (557 nm in dichloromethane) is shifted toward the shorter wavelength in the order of the binuclear adduct and the trinuclear. In the case of the trinuclear $(CuA)_2Cu(NO_3)_2$ adduct, the position is also shifted to the shorter wavelength compared to that of the parent CuA complex (545 nm in dichloromethane). It is well-known that the d–d absorption band of a copper(II) complex is shifted to the longer wavelength, as it is distorted from planar toward tetrahedral geometry. That is, the planarity of a copper(II) environment in CuSA or CuA is enhanced in the order of the parent complex, the binuclear adduct and the trinuclear.

Magnetic susceptibilities were also measured both for the $CuSACuCl_2$ and $(CuSA)_2Cu(NO_3)_2$ adducts in the range from liquid nitrogen temperature to room temperature. With using a Bleany–Bowers eqn. (1) for the binuclear adduct [15] as well as an eqn. (2) (which is applied to the linear trinuclear system) for the trinuclear adduct [5], the magnetic parameters were determined by the best-fit tech-

TABLE I. The Results of Elemental Analyses and Electronic Spectra of the Adducts

| Adducts | Elemental analyses (%)[a] | | | UV ($CH_2Cl_2$) $\lambda_{max}$ (nm) | Color |
|---|---|---|---|---|---|
| | C | H | N | | |
| $CuSACuCl_2$ | 38.16<br>(38.02) | 3.50<br>(3.65) | 6.14<br>(6.33) | 553 | brown |
| $(CuSA)_2Cu(NO_3)_2 \cdot 2H_2O$ | 40.25<br>(40.07) | 4.22<br>(4.32) | 9.95<br>(10.01) | 547 | brown |
| $(CuA)_2Cu(NO_3)_2 \cdot 2H_2O$ | 36.33<br>(36.25) | 4.66<br>(5.07) | 10.04<br>(10.57) | 524 | light green |
| $(CuS)_2Cu(NO_3)_2 \cdot 2THF$[b] | 48.98<br>(48.46) | 3.94<br>(4.47) | 8.91<br>(8.48) | | purple |
| $(CuSA)_2Ni(NO_3)_2 \cdot H_2O$ | 41.56<br>(41.19) | 4.12<br>(4.20) | 10.38<br>(10.29) | 555 | purple |
| $(CuSA)_2Zn(NO_3)_2$ | 41.83<br>(41.77) | 4.36<br>(4.01) | 10.37<br>(10.44) | 553 | reddish brown |

[a] The calculated values for elemental analyses are shown in parentheses.

[b] $(CuSA)_2Cu(NO_3)_2 \cdot 2THF$ scarcely dissolves into dichloromethane, and the spectrum was not obtained.

TABLE II. The Elemental Analyses, Electronic and Infrared Spectra of the Trinuclear Alkaline Earth(II) and Lanthanoid(III) Adducts

| Adducts | Elemental analyses (%)[a] | | | UV ($CH_2Cl_2$) $\lambda_{max}$ (nm) | IR $\nu(NO_3)$ ($cm^{-1}$) |
|---|---|---|---|---|---|
| | C | H | N | | |
| $(CuSA)_2Mg(NO_3)_2$ | 43.91 | 4.16 | 11.06 | 553 | 1730 |
| | (44.02) | (4.22) | (11.00) | | 1755 |
| $(CuSA)_2Ca(NO_3)_2 \cdot 0.5H_2O$ | 42.59 | 3.78 | 10.62 | 551 | 1743 |
| | (42.64) | (4.21) | (10.65) | | 1772 |
| $(CuSA)_2Sr(NO_3)_2$ | 40.72 | 4.04 | 9.34 | 554 | 1740 |
| | (40.65) | (3.90) | (10.16) | | 1759 |
| $(CuSA)_2Y(NO_3)_3$ | 37.84 | 3.95 | 10.71 | 553 | 1733 |
| | (37.76) | (3.62) | (11.01) | | 1764 |
| $(CuSA)_2La(NO_3)_3$ | 36.30 | 3.51 | 10.55 | 552 | 1736 |
| | (35.75) | (3.43) | (10.42) | | 1766 |
| $(CuSA)_2Nd(NO_3)_3$ | 35.95 | 3.49 | 10.29 | 553 | 1736 |
| | (35.55) | (3.41) | (10.37) | | 1766 |

[a]Calculated values are shown in parentheses. The adducts show light to dark purple colors.

nique: $g = 2.07$, $J = -30$ $cm^{-1}$, $N\alpha = 0$ for the binuclear adduct; $g = 2.05$, $J = -26$ $cm^{-1}$, $N\alpha = 0$ for the trinuclear adduct.

$$\chi_A = \frac{Ng^2\beta^2}{3\kappa T}\left[1 + \frac{1}{3}\exp(-2J/\kappa T)\right]^{-1} + N\alpha \qquad (1)$$

$$\chi_A = \frac{Ng^2\beta^2}{12\kappa T}\;\frac{\exp(2J/\kappa T) + 10\exp(3J/\kappa T) + 1}{\exp(2J/\kappa T) + 2\exp(3J/\kappa T) + 1} + N\alpha \qquad (2)$$

where $J$ is the exchange integral between the adjacent copper ions, and other symbols have their usual meanings. In general, the binuclear copper(II) adducts (e.g. $CuSCuCl_2$) show the maxima in the $\chi_A$ *vs.* $T$ curve, which is diagnostic for the binuclear structure. However, the $CuSACuCl_2$ adduct did not show the maximum within the experimental temperature range. It is reported that the binuclear $CuCl_2$ adduct with (*N,N*′-disalicylidene-1,3-propylenediaminato)-copper(II) does not show the maximum in the $\chi_A$ *vs.* $T$ curve [9]. The $J$ value of the adduct is $-49$ $cm^{-1}$, of which absolute value is extremely small compared to those of the binuclear adducts showing the maxima [9]. The strength of the antiferromagnetic interaction, or the magnitude of $J$, is affected by various factors; one of them is the stereochemistry about the oxygen bridges (the superexchange integral through oxygen bridges) [3]. As has been shown in the electronic spectra, the position of the d–d band of $CuSACuCl_2$ is largely shifted to the shorter wavelength compared to that of $CuSCuCl_2$ (565 nm), which exhibits that the planarity of the CuSA complex is greater than that of the CuS complex in the binuclear adducts. Sinn *et al.* reported that if one of the metals in the binuclear adduct is in the planar environment, the adjacent metal will be distorted away from planarity (vice versa) [16]. In view of the electronic spectra discussed above, the distortion of the copper(II) environment of $CuCl_2$ from planar toward tetrahedral symmetry might be greater in the $CuSACuCl_2$ adduct than in the $CuSCuCl_2$ adduct. This leads to the results that the superexchange integral through oxygen bridge is weaker in $CuSACuCl_2$ than in $CuSCuCl_2$, resulting in the smaller absolute $J$ value for the former; that is, the former does not show the maximum in the curve.

The CuSA complex also formed the trinuclear adducts with alkaline earth(II) and lanthanoid(III) nitrate (Table II). The adducts show the d–d bands at the almost same position as that of the CuSA complex. In the infrared spectra, two weak bands arising from N=O frequencies of a nitrate group were observed around 1750 $cm^{-1}$ in these adducts (Fig. 3

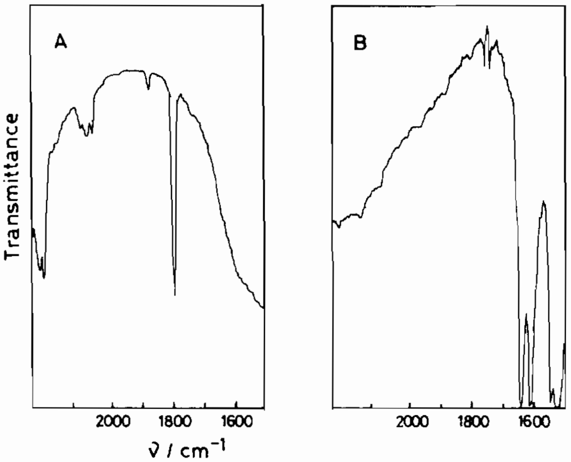


Fig. 3. The infrared spectra of calcium(II) nitrate tetrahydrate (a) and the $(CuSA)_2Ca(NO_3)_2$ adduct (b).

and Table II). It has been reported that the ionic nitrate group exhibits the band arising from the N=O frequency, whilst the coordinated nitrate group exhibits two bands with the bidentate coordination mode giving a wider separation of the two bands (20–66 $cm^{-1}$) than the monodentate one (5–26 $cm^{-1}$) [17]. In the present case, the separation of the bands is 20–30 $cm^{-1}$ (Table II), which confirms that the nitrate groups coordinate to the central metal(II, III) ions. However, from the above value of the separation, it is difficult to judge if the nitrate groups coordinate with the mono- or bidentate mode because the value is situated within the range of those values. In the trinuclear alkaline earth(II) adducts, the nitrate groups might coordinate with the monodentate mode because it is difficult for the calcium(II), magnesium(II) and strontium(II) ions to take a coordination number over six. The lanthanoid(III) adducts also show the two weak bands with almost the same separation as that of the alkaline earth(II) adducts. In the case of the lanthanoid(III) adducts, two structures might be possible; one is pentagonal bipyramidal and the other is octahedral. While in the former structure three nitrate groups can coordinate to the central lanthanoid(III) cation, two groups may coordinate in the latter, but the remaining one is ionic. The IR band for the ionic mode was not found in the adducts, which presumably supports the pentagonal bipyramidal structure. However, the exact structure might not be defined because the band for the ionic mode is so weak that it is sometimes overlooked.

As has been described above, the CuSA complex forms the binuclear adducts with copper(II) chloride, and also forms the trinuclear with some metal(II,III) nitrates. It has been also reported that copper(II) perchlorate forms the trinuclear adduct [8]. On the other hand, copper(II) acetate did not form the adducts with the CuSA complex. Thus, the counter anions of the metal salts must take an important role in the formation of the adducts. Further studies will be performed on the factors which control the formation of the bi- or trinuclear adduct.

## Acknowledgements

We wish to express our thanks to Dr. J. Takeuchi for his measurements of magnetic susceptibilities.

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