Thermochimica Acta, 189 (1991) 193–200
Elsevier Science Publishers B.V., Amsterdam

Thermal properties of α,ω-diaminoalkane adducts of bis-(3-nitro-2,4-pentanedionato)copper(II) in the solid phase

M. Fujiwara [a], H. Wakita [a] and T. Matsushita [b]

[a] *Department of Chemistry, Faculty of Science, Fukuoka University, Nanakuma, Jonan-ku, Fukuoka 814-01 (Japan)*

[b] *Department of Materials Chemistry, Faculty of Science and Technology, Ryukoku University, Seta, Otsu 520-21 (Japan)*

(Received 11 February 1991)

Abstract

α,ω-Diaminoalkane adducts of bis(3-nitro-2,4-pentanedionato)copper(II), where α,ω-diaminoalkanes can be 1,2-diaminoethane, 1,3-diaminopropane or 1,4-diaminobutane, have been isolated and characterised by spectroscopic methods and elemental analyses. It has been found that these adducts are converted to the corresponding tetra-aza macrocyclic copper(II) complexes in the solid phase. The reaction mechanism is discussed from the thermal properties of the adducts.

INTRODUCTION

Macrocyclic polyaza ligands and their metal complexes have been synthesised and investigated as models of porphyrins and their related compounds [1]. Many methods have been reported for the synthesis of macrocyclic polyaza compounds [2]; of these, a template method [3] has been shown to be very useful, because macrocyclic metal complexes can be obtained by the reaction of dicarbonyl compounds and diamines in the presence of a suitable metal ion and, in general, their yields are high. However, these reactions took place in solution. Recently, we have reported that the 1,2-diaminoethane adduct of bis(3-nitro-2,4-pentanedionato)copper(II), $Cu(3\text{-}NO_2acac)_2 \cdot en_2$, can be converted to the corresponding tetra-aza macrocyclic complex, $Cu(NO_2\text{-}N_4[14])$, by heating it in the solid state [4].

In this paper, we describe the preparation and characterisation of the diamine adducts of $Cu(3\text{-}NO_2acac)_2$, $Cu(3\text{-}NO_2acac)_2 \cdot L_2$, where L can be 1,2-diaminoethane (en), 1,3-diaminoopropane (tn) or 1,4-diaminobutane (bn). In addition, the template reaction mechanism for the present solid system is discussed on the basis of the thermal properties of these diamine adducts.

0040-6031/91/$03.50

EXPERIMENTAL

Measurements

Diffuse reflectance spectra were recorded on a Hitachi 340 recording spectrophotometer. IR spectra were recorded on a Hitachi 215 grating spectrophotometer for the 4000–200 cm^{-1} region. Thermogravimetric and differential scanning calorimetric analyses were made in a nitrogen stream at a heating rate of 2 °C/min^{-1} using a Rigaku Denki thermal analyser, Model 8002.

Preparation of copper(II) complexes and diamine adducts

The copper(II) complexes, bis(3-nitro-2,4-pentanedionato)copper(II), $Cu(3\text{-}NO_2acac)_2$, the 14-membered tetra-aza macrocyclic copper(II) complex, $Cu(NO_2\text{-}N_4[14])$, and the diamine adducts of $Cu(3\text{-}NO_2acac)_2$, $Cu(3\text{-}NO_2acac)_2 \cdot (diamine)_2$, were prepared according to the procedures described in the previous papers [4,5].

The preparative scheme for the copper(II) complexes is shown in Fig. 1.

RESULTS AND DISCUSSION

IR spectra

Figure 2 shows the IR spectra of the parent complex, $Cu(3\text{-}NO_2acac)_2$, its 1,2-diaminoethane adduct, $Cu(3\text{-}NO_2acac)_2 \cdot en_2$, and the 14-membered tetra-aza macrocyclic complex, $Cu(NO_2\text{-}N_4[14])$, measured in KBr discs. The spectrum of the parent complex exhibits characteristic bands at 1585 and 1520 cm^{-1} due to C=O and C=C stretching vibrations. In the spectrum of the 1,2-diaminoethane adduct, characteristic bands due to 1,2-diaminoethane appear at 3250 (ν(NH)), 1660 (δ(NH)), 1310 (ν(C–C)), 1280 (ν(C–N)), and at 1090 and 1045 cm^{-1} (δ(C–H)). Other absorption bands observed at 1590, 1525, 1400, 1345, 1115, 960 and 830 cm^{-1} are similar to those observed for the parent complex, but are shifted slightly to higher frequencies by about 5–10 cm^{-1}. These bands are due to the coordinated

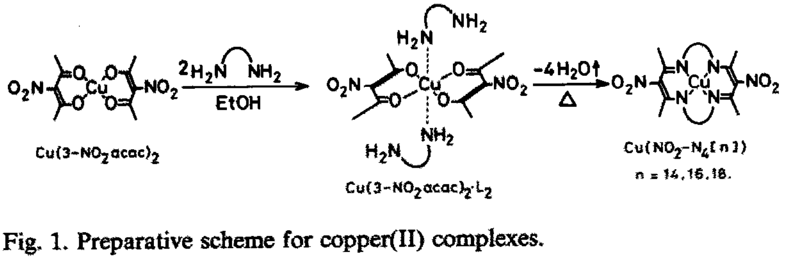

Fig. 1. Preparative scheme for copper(II) complexes.

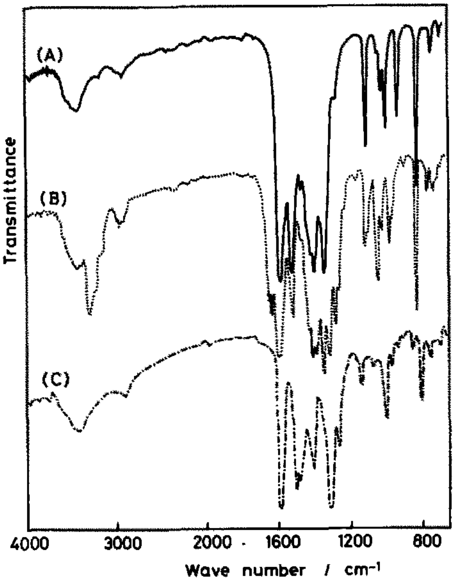

Fig. 2. IR spectra of $Cu(3\text{-}NO_2acac)_2$ (curve A), its 1,2-diaminoethane adduct (curve B) and the 14-membered tetra-aza macrocyclic complex (curve C).

3-nitro-2,4-pentanedionato groups. From a comparison of the IR spectra, it can be concluded that no significant change takes place on the coordinated β-diketonato groups, between the parent complex and the diamine adduct. The small shifts to higher frequencies due to the β-diketonato groups, which were observed for the diamino adduct, may be caused by an increase in electron density on the central copper(II) ion induced by the coordination of 1,2-diaminoethanes. This would tend to weaken the coordinate bonds between the metal ion and the β-diketonato groups.

In the IR spectrum of the 14-membered macrocyclic complex, the bands due to amino groups disappear, and a strong band appears at 1560 cm^{-1}. This is assigned to the conjugated stretching vibrations of C=N and C=C.

Figure 3 shows the IR spectra of the above three complexes in the lower frequency (800–300 cm^{-1}) region, measured by using a demountable cell with polyethylene film. The powdered sample was mixed to form a paste with a little Nujol. The spectrum of the parent complex has strong bands at 608, 458 and 444 cm^{-1}. These can be assigned to a combination of Cu–O stretching and ring-deformation vibrations. The diamine adduct exhibits strong bands at 580 and 420 cm^{-1} in addition to a new band at 380 cm^{-1}. The former can be assigned to Cu–O stretching vibrations and the latter to Cu–N stretching vibrations [6]. The shift to lower frequencies for the former bands, by around 30 cm^{-1}, is consistent with the argument described above. On the other hand, the macrocyclic complex exhibits a strong band at 456 cm^{-1}, which can be assigned to Cu–N stretching vibrations. The shift to higher frequency, by around 80 cm^{-1} compared to that of the diamine

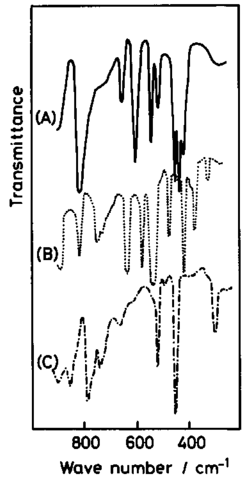

Fig. 3. Far-IR spectra of Cu(3-NO_2acac)$_2$ (curve A), its 1,2-diaminoethane adduct (curve B) and the 14-membered tetra-aza macrocyclic complex (curve C).

adduct, indicates that the coordinate bonds between the central copper(II) ion and the nitrogen atoms of the macrocyclic moiety are stronger than those in the diamine adduct.

Reflectance spectra

In order to obtain information on the electronic states of the central copper(II) ion in the parent complex and in its diamine adducts, their

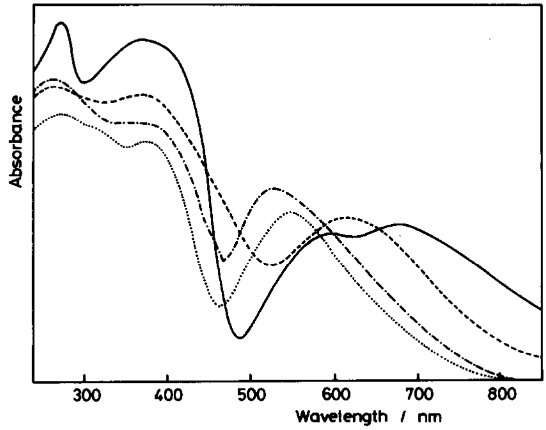

Fig. 4. Reflectance spectra of Cu(3-NO_2acac)$_2$ and its diamine adducts: (———), Cu(3-NO_2acac)$_2$; (·–·–·–·), Cu(3-NO_2acac)$_2$·en$_2$; (······), Cu(3-NO_2acac)$_2$·tn$_2$; (— — —), Cu(3-NO_2acac)$_2$·bn$_2$.

reflectance spectra were measured in the solid phase (Fig. 4). The spectrum of the parent complex has four absorption bands at 664 (strong), 590 (weak), 364 and 272 nm. That of the 1,2-diaminoethane adduct has three absorption bands at 527, at around 360 and at 265 nm. Although the band positions in the UV region are almost identical, those in the visible region are different: the absorption peak of $Cu(3\text{-}NO_2acac)_2 \cdot en_2$ is shifted to shorter wavelengths by about 140 nm, compared to the strong peak of the parent complex. The absorption bands of the 1,3-diaminopropane (549 nm) and 1,4-diaminobutane (612 nm) adducts in the visible region are also shifted to shorter wavelengths by about 115 and 52 nm, respectively, compared to the strong peak of the parent complex. These shift values are smaller than that observed in the case of 1,2-diaminoethane and may arise from coordination of the diamine molecules to the parent complex. Therefore, it can be concluded that coordination bonds between diamines and copper(II) ion are stronger in the order: 1,2-diaminoethane > 1,3-diaminopropane ≫ 1,4-diaminobutane.

Thermal properties of diamine adducts of $Cu(3\text{-}NO_2acac)_2$

The diamine adducts of $Cu(3\text{-}NO_2acac)_2$ may be considered to be intermediates in the template reaction forming tetra-aza macrocyclic complexes. As reported in our preliminary paper [4], $Cu(3\text{-}NO_2acac)_2 \cdot en_2$ could be converted to the corresponding tetra-aza macrocyclic complex by heating in the solid state. Therefore, the thermal behaviour of the diamine adducts were examined by TG–DSC analysis. Figure 5 shows the TG–DSC curves obtained for $Cu(3\text{-}NO_2acac)_2 \cdot en_2$. The DSC curve has two exothermic peaks. The first peak at the reaction time of 60 min is accompanied by a

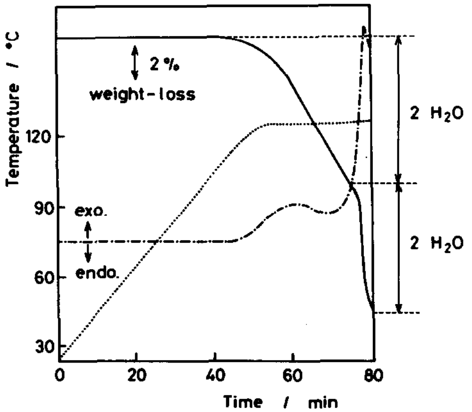

Fig. 5. TG–DSC curves of $Cu(3\text{-}NO_2acac)_2 \cdot en_2$: (———), TG curve; (·—·—·—·), DSC curve; (······), temperature.

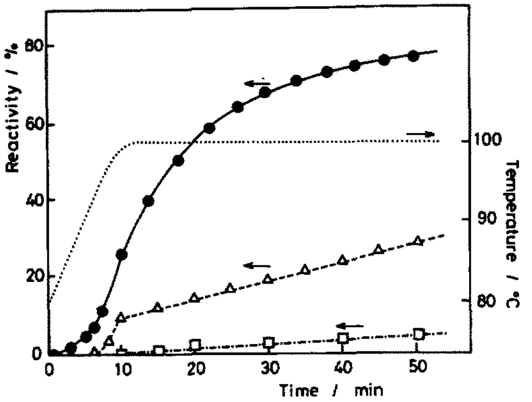

Fig. 6. Reactivity of diamine adducts on thermal condensation: (□), Cu(3-NO_2acac)$_2$·en$_2$; (△), Cu(3-NO_2acac)$_2$·tn$_2$; (●), Cu(3-NO_2acac)$_2$·bn$_2$; (······), temperature.

weight loss of 7.4% in the TG curve. This value agrees well with the value calculated (7.64%) assuming that two moles of H_2O are eliminated from one mole of adduct. The second peak of the DSC curve, at the reaction time of 78 min, is very sharp and is accompanied by a weight loss of 15.3%, which agrees well with the value calculated (15.27%) assuming that four moles of H_2O are eliminated from one mole of adduct.

The dark brown copper(II) complex obtained after heating to 120 °C for around 2 hours was identified as Cu(NO_2-N_4[14]) from spectroscopic data (visible absorption and IR spectra) and elemental analysis. These results indicate that two Schiff-base bonds between the coordinated carbonyl groups and the uncoordinated, free amine moieties were formed at the first step, followed by formation of an additional two Schiff-base bonds between the coordinated carbonyl groups and the coordinated amine moieties at the second step.

Figure 6 shows a comparison of the reactivities of the diamine adducts on thermal condensation. The reactivity was estimated from plots of the percentage weight loss of each adduct with respect to the calculated value based on the assumption that four moles of H_2O per mole of adduct are eliminated, as a function of time. The heating rate was 2 °C min^{-1} and the reaction temperature was held at 100 °C. As the thermal reaction of Cu(3-NO_2acac)$_2$ · en$_2$ takes place above 100 °C, its weight loss is very small. For Cu(3-NO_2acac)$_2$ · tn$_2$, the thermal reaction begins at 91 °C, and its weight loss is larger than that of Cu(3-NO_2acac)$_2$ · en$_2$. On the other hand, the thermal reaction of Cu(3-NO_2acac)$_2$ · bn$_2$ begins at 82 °C and its weight loss is the largest of the three adducts. It can be seen that the lower the initiation temperature of the thermal reaction, the higher the reactivity of the adducts. Therefore, the thermal reactivity of the adducts is found to increase in the order: Cu(3-NO_2acac)$_2$ · en$_2$ < Cu(3-NO_2acac)$_2$ · tn$_2$ < Cu(3-NO_2acac)$_2$ · bn$_2$.

Intramolecular condensation of diamine adducts in the solid phase

All three diamine adducts of $Cu(3\text{-}NO_2acac)_2$ have been found to undergo a two-step exothermic change on heating in the solid phase, accompanied by elimination of four moles of H_2O per mole of adduct. The two exothermic DSC peaks were observed at 108 and 115°C for $Cu(3\text{-}NO_2acac)_2 \cdot tn_2$, and at 94 and 98°C for $Cu(3\text{-}NO_2acac)_2 \cdot bn_2$.

In our previous paper [5], we discussed the mechanism of the intramolecular condensation of these diamine adducts in solution. It should be noted that even in the solid phase, almost the same condensation reaction might occur. During the first stage, the uncoordinated, free amine moieties may attack the carbonyl carbons of the coordinated 3-nitro-2,4-pentanedionato groups to form two Schiff-base bonds. At the second stage, the coordinate bonds between the copper(II) ion and the coordinated amine moieties may cleave, followed by the nucleophilic attack of these free amines on the residual carbonyl carbons to form an additional two Schiff-base bonds and, subsequently, to produce the corresponding tetra-aza macrocyclic copper(II) complex. In this reaction process, the nitro groups of the coordinated β-diketonato ions may play an important role in both the first and second steps. Because the nitro group is a strong electron-withdrawing group, it may contribute to stabilisation of the coordinate bonds between the diamines and the central copper(II) ion. This leads to intramolecular condensation by preventing the elimination of the coordinated diamines when the diamine adducts are heated. In fact, it has been reported that in the thermal reaction of the 1,2-diaminoethane adduct of $Cu(acac)_2$, only the elimination of the diamines was observed [7]. Moreover, the nitro group should cause a decrease in the electron density on the coordinated carbonyl carbons. This may facilitate nucleophilic attack by the uncoordinated, free amine moieties on the nitro groups.

As shown in Fig. 5, the first exothermic reaction takes place relatively slowly, and the second one vigorously. This may be explained in terms of the steric configuration of the diamine adducts. In the first condensation reaction, because the coordinate bonds between the central copper(II) ion and the amino groups must restrict mobility of other free amine moieties of the diamines, their reactivities toward the carbonyl groups may be lowered. In the second condensation reaction, because the free amine moieties, which are formed by cleavage of the coordinate bonds, can be positioned close to the residual, coordinated, carbonyl groups, the reaction may occur more readily.

Thus, we have demonstrated that isolation of the copper(II) complexes with the tetra-aza macrocycles is possible by thermal reaction of the diamine adducts of $Cu(3\text{-}NO_2acac)_2$ in the solid state, provided that heating of the system can be ceased when the weight loss of the adducts reaches the calculated value based on the elimination of four moles of H_2O per mole of adduct. Therefore, the thermal template reaction in the solid phase is considered to be very valuable for synthesising tetra-aza macrocyclic complexes, compared with that in solution, because intermolecular reaction is restricted in the solid phase, thus resulting in higher yields.

REFERENCES

1 D.H. Busch, D.G. Pillsbury, F.V. Lovecchio, A.M. Tait, Y. Hung, S. Jackels, M.C. Rakowski, W.P. Schammel and Y.L. Martin, in D.T. Sawyer (Ed.), Electrochemical Studies of Biological Systems, ACS Symposium Series, Vol. 38, American Chemical Society, Washington, D.C., 1977.
2 G.A. Melson, Coordination Chemistry of Macrocyclic Compounds, Plenum Press, New York, 1979.
3 M. Green, J. Smith and P.A. Tasker, Inorg. Chim. Acta, 5 (1971) 17.
D.St.C. Black and G.I. Moss, Aust. J. Chem., 40 (1987) 129.
4 M. Fujiwara, S. Kinoshita, H. Wakita, T. Matsushita and T. Shono, Chem. Lett., (1987) 1323.
5 M. Fujiwara, H. Wakita and T. Matsushita, Polyhedron, submitted.
6 K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, Wiley, New York, 1970.
7 T. Kurauchi, M. Matsui, Y. Nakamura, S. Ooi, S. Kawaguchi and H. Kuroya, Bull. Chem. Soc. Jpn., 47 (1974) 3049.