

This article was downloaded by:

On: 23 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455674>

### THE NUCLEOPHILIC RING SUBSTITUTION OF (3-BROMO-2,4-PENTANEDIONATO)COPPER(II)

Kuninobu Kasuga<sup>a</sup>; Takeo Nagahara<sup>a</sup>; Yasuo Yamamoto<sup>a</sup>

<sup>a</sup> Department of Chemistry, Faculty of Science, Shimane University, Matsue, Japan

**To cite this Article** Kasuga, Kuninobu , Nagahara, Takeo and Yamamoto, Yasuo(1980) 'THE NUCLEOPHILIC RING SUBSTITUTION OF (3-BROMO-2,4-PENTANEDIONATO)COPPER(II)', *Journal of Coordination Chemistry*, 10: 4, 217 – 218

**To link to this Article:** DOI: 10.1080/00958978008079865

**URL:** <http://dx.doi.org/10.1080/00958978008079865>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## THE NUCLEOPHILIC RING SUBSTITUTION OF (3-BROMO-2,4-PENTANEDIONATO)COPPER(II)

KUNINOBU KASUGA, TAKEO NAGAHARA and YASUO YAMAMOTO

Department of Chemistry, Faculty of Science, Shimane University, Matsue 690, Japan

(Received February 28, 1980)

While the bromine atom of bis(3-bromo-2,4-pentanedionato)-copper(II) could not be substituted for nucleophiles such as succinimide, phthalimide, phenol, and benzenethiol, the salts of these nucleophiles produced bis(3-substituted 2,4-pentanedionato)-copper(II) complexes

### INTRODUCTION

The substitution reaction on the ligand parts of metal complexes has become important for their catalytic actions and also for the fundamental study of the enzyme reactions controlled by metal ions.<sup>1</sup> In certain metal acetylacetonates, consideration of the proposed aromaticity suggested that these complexes might undergo an electrophilic substitution on their chelate rings.<sup>2,3</sup> The first report of the electrophilic substitution of metal acetylacetonate was the bromination of chromium(III) acetylacetonate by the action of bromine in chloroform.<sup>4</sup> Subsequently, a nitro derivative of copper(II) acetylacetonate was published.<sup>5</sup> Kluiber also reported the bromination and sulfonyl chlorination of a few metal acetylacetonates.<sup>6</sup> Collman and his coworkers did an intensive study of the electrophilic substitution of metal acetylacetonates.<sup>7</sup> Furthermore, they tried a nucleophilic displacement of tris(3-halogeno-2,4-pentanedionato)-chromium(III) by various nucleophiles such as sodium ethoxide, sodium azide, potassium acetate, sodium nitrate, potassium iodide, and zinc powder, but the halogen atom could not be displaced by any nucleophiles.<sup>7b</sup> Recently, a nucleophilic substitution of metal acetylacetonate derivatives of iron(III), aluminum(III), and beryllium(II) with nucleophiles such as sodium salts of succinimide, phthalimide, phenol, and benzenethiol have been reported from our laboratory.<sup>8</sup> Yoshida *et al.* also succeeded in the nucleophilic substitution of the halogen atom of tris(3-halogeno-2,4-pentanedionato)-metal(III) for benzenethiol and its derivatives.<sup>9</sup> We report here the nucleophilic substitution reaction of bis(3-bromo-2,4-pentanedionato)copper(II). The bromine atom of bis(3-bromo-2,4-pentanedionato)-

copper(II) was substituted for nucleophiles such as sodium salts of succinimide, phthalimide, phenol, and benzenethiol. On the other hand, bases such as succinimide, phthalimide, and phenol did not substitute for the bromine atom of the complex. Benzenethiol also caused a reduction of copper(II) of the complex even at low temperature in ordinary organic solvents, and a substituted compound could not be obtained.

In the study of infrared spectra of metal acetylacetonate derivatives, Nakamoto and Martell assigned the band of  $1580\text{ cm}^{-1}$  of bis(2,4-pentanedionato)-copper(II) to a C=C stretching vibration.<sup>3</sup> From the data given in Table I, we can see that C=C bands of the succinimido and phthalimido substituted compounds are shifted to higher frequencies than that of bis(2,4-pentanedionato)copper(II) in spite of the large masses of their substituent groups. This might result from the strong plus inductive effect of

TABLE I  
The IR spectral data of the bis(3-substituted 2,4-pentanedionato)copper(II) complexes

(acacX) <sub>2</sub> Cu(II) <sup>a</sup> X =	Relative mass of the substituents	IR <sup>b</sup> (cm <sup>-1</sup> , KBr pellets)
H	1	1580
Cl	35.5	1577
Br	80	1556
phenoxy	93	1555
succinimido	98	1591
phenylthio	109	1552
phthalimido	146	1596

<sup>a</sup>acacX = 3-substituted 2,4-pentanedionanion.

<sup>b</sup>The bands of the C=C stretching vibration.

these substituent groups which strengthen a C=C bonding of the chelate ring, as is seen in the case of the metal(II) hexafluoroacetylacetonate complexes.<sup>10</sup>

## EXPERIMENTAL

The 3-position carbon of bis(2,4-pentanedionato)copper(II) was brominated according to the procedure of Collman *et al.*<sup>7b</sup>

### *Bis(3-succinimido-2,4-pentanedionato)copper(II)*

A mixture of succinimide (0.060 g, 0.006 mol) and sodium hydroxide (0.24 g, 0.006 mol) in methanol was heated on a water bath and the solution was concentrated until tarry precipitates were formed. A 100 ml dichloromethane solution of bis(3-bromo-2,4-pentanedionato)copper(II) (0.84 g, 0.002 mol) was added to the 3 ml methanol solution containing tarry sodium succinimide and was allowed to stand for 3 days with stirring at room temperature. The formed precipitates were filtered off and the filtrate was evaporated under a reduced pressure. The residue was recrystallized from dichloromethane and methanol, yielding the blue powder; yield, 16% (based on the bromo substituted compound). IR, 1702 cm<sup>-1</sup> (C=O of a succinimido group). Anal. Calcd. for C<sub>18</sub>H<sub>20</sub>O<sub>8</sub>N<sub>2</sub>Cu: C,47.42; H,4.42; N,6.14. Found: C,47.73; H,4.24; N,6.15.

### *Bis(3-phthalimido-2,4-pentanedionato)copper(II)*

The pale blue phthalimido substituted compound was obtained by the same treatment as that of the succinimido compound; yield, 15% (based on the bromo substituted compound). IR, 1715 cm<sup>-1</sup> (C=O of a phthalimido group). Anal. Calcd. for C<sub>26</sub>H<sub>20</sub>O<sub>8</sub>N<sub>2</sub>Cu: C,56.57; H,3.65; N,5.07. Found: C,56.56; H,3.75; N,4.75.

### *Bis(3-phenoxy-2,4-pentanedionato)copper(II)*

A mixture of bis(3-bromo-2,4-pentanedionato)copper(II) (0.84 g, 0.002 mol) and sodium phenoxide (1.40 g, 0.012 mol) in 100 ml dichloromethane was allowed to stand for 4 days with stirring at room temperature. The formed precipitates were filtered off and the filtrate was concentrated. The residue was recrystallized from dichloromethane and methanol, yielding the dark green powder of the phenoxy substituted compound; yield, 25% (based on the bromo substituted compound). IR, 1595 cm<sup>-1</sup> (a benzene ring of a phenoxy group). Anal. Calcd. for

C<sub>22</sub>H<sub>22</sub>O<sub>6</sub>Cu: C,59.26; H,4.97; Found: C,58.93; H,5.38.

### *Bis(3-phenylthio-2,4-pentanedionato)copper(II)*

A mixture of bis(3-bromo-2,4-pentanedionato)copper(II) (0.84 g, 0.002 mol) and sodium benzenethiolate (0.79 g, 0.006 mol) in 100 ml dichloromethane was allowed to stand for one day with stirring at room temperature. After the formed precipitates were filtered off, the filtrate was concentrated and the residue was dissolved in 20 ml chloroform. This solution was passed through a column of silica gel and a yellowish green elute was concentrated under a reduced pressure, yielding the yellowish green phenylthio substituted compound; yield, 35% (based on the bromo substituted compound). IR, 1580 cm<sup>-1</sup> (the benzene ring of a phenylthio group). Anal. Calcd. for C<sub>22</sub>H<sub>22</sub>O<sub>4</sub>S<sub>2</sub>Cu: C,55.27; H,4.64. Found: C,55.15; H,4.78.

## Measurements

The infrared spectra using KBr pellets were measured on a Hitachi 215-type spectrophotometer and a Shimadzu IR-27G spectrophotometer. The elemental analyses were carried out by means of a Yanagimoto MT 2 CHN Corder.

## REFERENCES

1. a) M. M. Jones, *Ligand Reactivity and Catalysis*, Academic Press Inc., 1968. b) R. H. Holm, *Inorganic Biochemistry*, vol. 2, G. L. Eichorn (ed), Elsevier Sci. Publ., Amsterdam (1973), p.1137. c) A. Nakahara, O. Yamanouchi, and Y. Nakao, *Bioorganic Chemistry*, vol. 4, E. E. Van Tamelen (ed), Academic Press (1978), p.349.
2. M. Calvin and K. W. Wilson, *J. Am. Chem. Soc.*, **67**, 2003 (1945).
3. K. Nakamoto and A. E. Martell, *J. Chem. Phys.*, **32**, 588 (1960).
4. H. Reihlen, R. Illig and R. Wittig, *Ber.*, **58B**, 12 (1925).
5. C. Djoidjeric, J. Lewis and R. S. Nyholm, *Chem. Ind. (London)*, 1959, 122.
6. a) R. W. Klüber, *J. Am. Chem. Soc.*, **82**, 4839 (1960). b) R. W. Klüber, *J. Am. Chem. Soc.*, **83**, 3030 (1961).
7. a) J. P. Collman, R. A. Moss, S. D. Goldby and V. S. Tvhanousky, *Chem. Ind. (London)*, 1960, 1213. b) J. P. Collman, R. A. Moss, H. Maltz and C. C. Heindel, *J. Am. Chem. Soc.*, **83**, 531 (1961). c) J. P. Collman, *Angew. Chem.*, **77**, 154 (1965).
8. a) Y. Yamamoto, K. Kasuga and A. Sumita, *Bull. Chem. Soc. Jpn.*, **49**, 2021 (1976). b) K. Kasuga, M. Anami and Y. Yamamoto, *Bull. Chem. Soc. Jpn.*, **51**, 476 (1978).
9. Z. Yoshida, H. Ogoshi and Y. Shimizu, *Kogyo Kagaku Zasshi*, **72**, 1648 (1969).
10. K. Nakamoto, Y. Morimoto and A. E. Martell, *J. Phys. Chem.*, **66**, 346 (1962).