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COPPER(II) COMPLEXES WITH *N,N'*-BIS(ALKYLAMINOALKYL)-OXAMIDES AND RELATED LIGANDS

H. OJIMA and K. NONOYAMA
Department of Chemistry, Aichi Kyoiku University, Kariya, 448 (Japan)

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CONTENTS

A. INTRODUCTION

The oxamide dianion acts as a bidentate ligand and, like the oxalate dianion, is also capable of coordinating as a bridging ligand to give many kinds of binuclear complexes. The binuclear copper(II) complexes formed by the oxamide dianion are more stable than those formed by the oxalate dianion, owing to the high extent of magnetic interaction between two metal ions, especially in the *N,N'*-bis(coordinating group substituted)oxamides. It is hoped that the binuclear complexes formed by the *N,N'*-bis(coordinating group substituted) oxamides will lead to the development of a new field of coordination chemistry.

A review, "Coordination Properties of Amide Bond" has already been published [1]. The present paper introduces copper(II) complexes with the oxamide dianion and its derivatives not covered by the previous review.

B. ACID DISSOCIATION OF AMIDE PROMOTED BY METAL ION

The amide nitrogen in a common amide has already lost its function as a base owing to the "Aufrichtung" of the adjoining carbonyl group. It behaves

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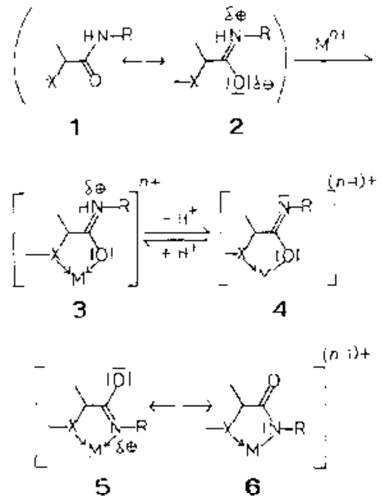


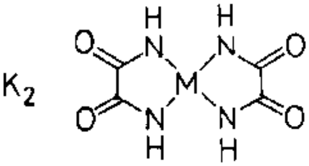
Fig. 1. Acid dissociation of amide promoted by metal ion.

rather as a weak acid. Most amides are neutral throughout the pH range. However, if the amide possesses another coordinating group at a position which can form a 5- or 6-membered chelate, and a heavy metal ion is also present, the amide dissociates and coordinates simultaneously in an unexpectedly low pH range [2,3] (cf. Fig. 1), i.e. **2** is capable of coordinating to a metal ion in neutral and slightly acidic solution, as shown in formula **3**. The nitrogen atom in **3** tends to be positively charged and promotes acid dissociation of the amide under mild conditions (pH 7). If the resonance equilibrium, **5** ↔ **6**, exists, this may stabilize the chelate ring. In the case of the oxamide, especially in the *N,N'*-bis(coordinating group substituted) oxamide, such a tendency is promoted owing to the strong chelate effect. When the amide nitrogen coordinates to a metal ion, it is sp^2 hybridized to conjugate with $p\pi$ electrons of the carbonyl group. In the case of the oxamide dianion, the carbonyl oxygen can coordinate to another metal ion to form a binuclear system. The presence of an effective π-path between the two metal ions is the reason why complexes thus formed show such strong magnetic interaction in spite of the two metal ions being divided by three atoms.

C. COPPER(II) COMPLEXES WITH THE OXAMIDE DIANION

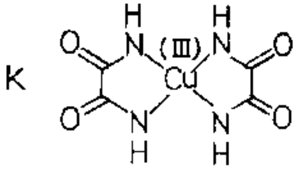
Hoffmann and Ehrhardt [4] were the first to obtain copper(II) and nickel(II) complexes with the oxamide dianion. **7**. Then Rising et al. [5], and Poddubnaya and Gabrilov [6] noted that these complexes were invariably contaminated with the free ligand and the decomposed products of the complex, and only poor analytical results could be obtained. This may be because the complexes are hydrolysed very easily in an aqueous solution and that oxamide itself hydrolyses in alkaline solution. An IR study of bis(oxamido)copper(II) and bis(oxamido)nickel(II) was carried out by Kuroda et al. [7]. Then Armendarez and Nakamoto [8] presented an accurate assignment of the IR spectra of the bis(oxamido)copper(II), bis(oxamido)nickel(II) and bis(oxamido)palladium(II) using pure samples prepared by an improved synthetic method [8].

Following electro-oxidation of complex **7** (M = Cu(II)) in 0.1 N KOH (0.55 V vs. the standard calomel electrode (SCE)), the bis(oxamido)copper (III), **8**, was isolated and characterized by spectrophotometric and magnetic susceptibility measurements [9]. Such a high oxidation state is stabilized [9] because the oxamide dianion has very strong electron-donating capacity. The complexes, K[M(3-alkylbiuret^{2})$_2$] (M = Cu(III) and Ni(III)), were also isolated [9].



M = Cu(II), Ni(II), Pd(II)

7



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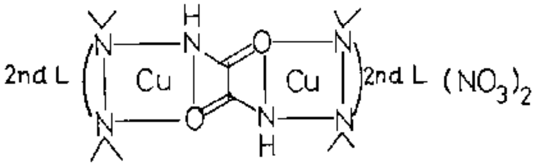
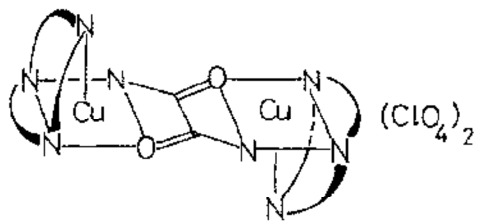
Although the oxamide dianion itself coordinates only in a strongly alkaline solution, stable mixed-ligand complexes may be formed in the presence of suitable additional ligands in a remarkably low pH range [10]. In these complexes, the oxamide dianion behaves as a bridging ligand, and the additional ligands force the complexes formed to adopt four types of coordination configurations as shown below [10]:



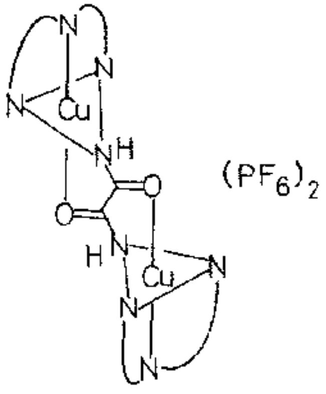
2nd ligand : *N*,*N*,*N'*,*N'*-tetramethylethylenediamine
2,2'-bipyridine
2-aminoethylpyridine

9



2nd ligand : $\text{-NH-(CH}_2)_3\text{-NH-(CH}_2)_3\text{-NH-(CH}_2)_4\text{-}$

10



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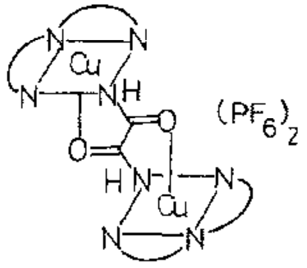
2nd ligand : *N*,*N*,*N*′,*N*″,*N*″-pentaethyldiethylenetriamine



12

2nd ligand : *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine

These configurations were derived from the results of spectrophotometric and magnetic susceptibility measurements. The behaviour of oxalato complexes [11–13] was also instructive in deriving these configurations. Comparative data (Fig. 2) show that the extent of magnetic interaction follows the order oxamido > oxamato > oxalato complex, reflecting that the amide dianion is the most advantageous ligand to set up the π path [10].

D. COPPER(II) COMPLEXES WITH *N*,*N*′-BIS(SUBSTITUENT)OXAMIDES

The ligands discussed in this paper are displayed in Table 1. Most of them were obtained by reaction of 1 mol diethyl oxalate with 2 mol or 1 mol of

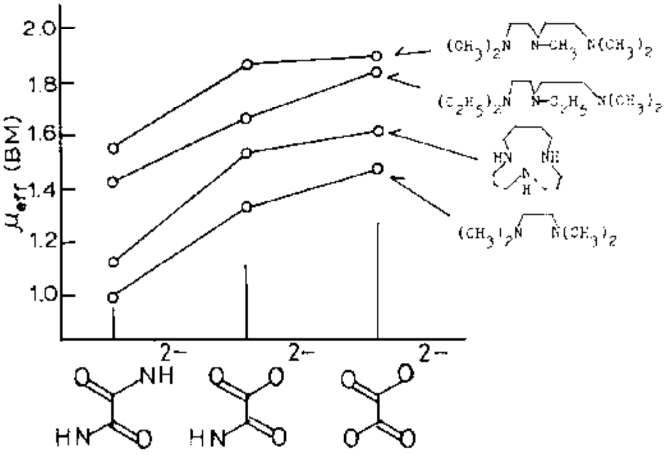
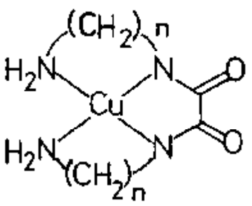


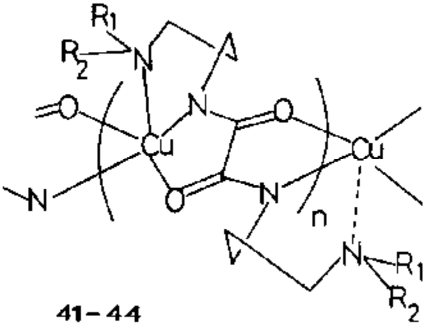
Fig. 2. The influence of second ligands on the μ_{eff} values of amido, oxamato and oxalato dicopper(II) complexes.

the corresponding amine. In general, these reactions proceeded faster and gave higher yields than in the case of the monoamides.

Ligands **13**, **14** and **15** (in each ligand, $R_1 = R_2 = H$ only) gave violet or reddish violet crystals of a complex of type **40** at pH 8 and higher [14]. However, ligands **13**, **14** and **15** ($R_1 = H$, $R_2 = CH_3$; $R_1 = R_2 = CH_3$; $R_1 = R_2 = C_2H_5$ etc.) did not form type **40** complexes, but gave green or olive-coloured crystals of component $[CuL^{2-}]$ which show subnormal μ_{eff} values. The polymeric structures **41**–**44** were proposed [15].



40



41–44

R_1	R_2	μ_{eff}(BM)	No.
H	CH_3	1.62	**41**
CH_3	CH_3	1.20	**42**
C_2H_5	C_2H_5	1.08	**43**
C_4H_9	C_4H_9	–	**44**

The complexes of type **40** undergo structural change with change in pH as shown in Fig. 3 [10]. Structure **c** is detectable by the Evans method ($\mu_{eff} = 1.4$–1.6) and could easily be isolated by replacement of H_2O with Cl^-. The reason why **c** is stabilized may be due to a π path such as Cu—O—C—N—Cu. A small difference in behaviour between structures with $n = 2$ and $n = 3$ in **40** is that the structure with $n = 3$ resists strong alkali to maintain **d** which does not change to **e**.

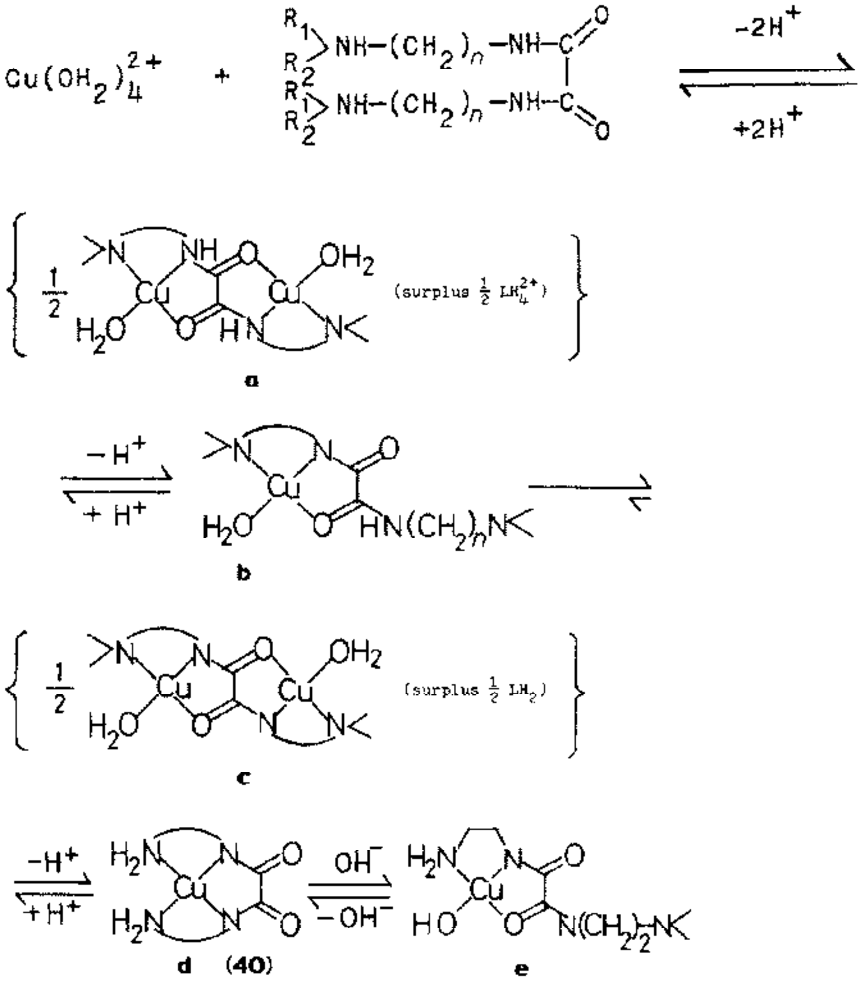
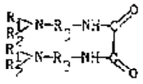
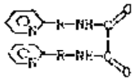
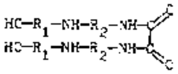
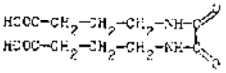
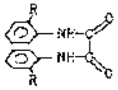
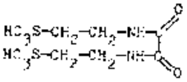
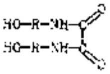
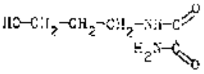
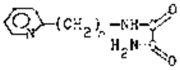
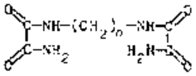
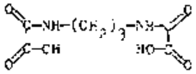
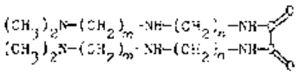


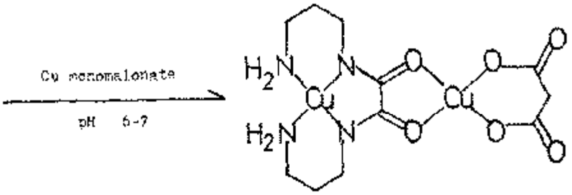
Fig. 3. The scheme of structural change in the oxamide–Cu^{2+} system depending upon pH.

TABLE 1

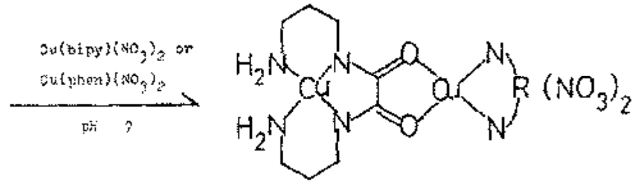
Oxamide ligands

Ligand		Number
	R_3 = $-CH_2-CH_2-$ $-CH(CH_3)-CH_2-$ $-CH_2-CH_2-CH_2-$	**13** **14** **15**
	R = $-CH_2-$ $-CH_2-CH_2-$	**16** **17**
	R_1, R_2 = $-(CH_2)_2-$, $-(CH_2)_3-$ $-(CH_2)_3-$, $-(CH_2)_2-$ $-CH(CH_3)-CH_2-$, $-(CH_2)_2-$	**18** **19** **20**
		**21**
	R = $-COOH$ $-\underset{X}{C}=O$	**22**
		**23**
	R = $-CH_2-CH_2-$ $-CH(CH_3)-CH_2-$ $-CH_2-CH_2-CH_2-$	**24** **25** **26**
		**27**
		**28**
	$n=2$ $n=3$	**29** **30**
		**31**
	m, n = 2, 2 3, 2 2, 3 3, 3 2, 4 3, 4 2, 6 3, 6	**32** **33** **34** **35** **36** **37** **38** **39**

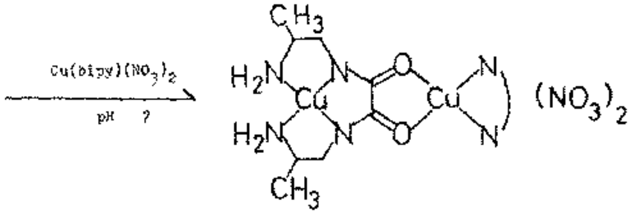
Complexes of type **40** (both $n = 2$ and 3, but $R_1 = R_2 = H$) gave binuclear complexes **45**–**49** on reaction with other complexes [16,17]:



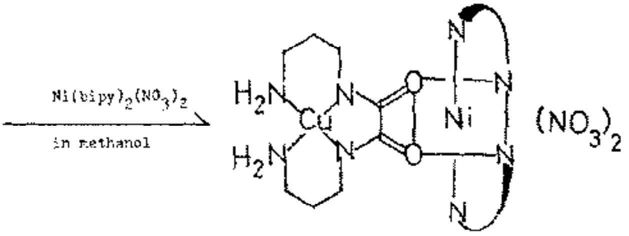
1.26 BM **45**



R : bipyridine 1.23 BM **46**
phenanthroline 1.22 BM **47**



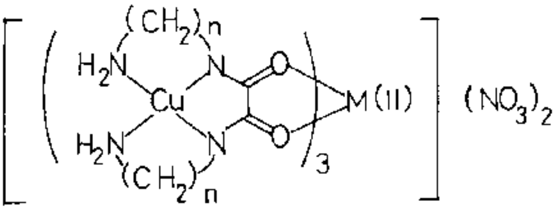
0.92 BM
48



Existence of magnetic interaction between Cu and Ni was recognized[17]

49

The complexes **50–52** were isolated [18]. The results from cryomagnetic investigation demonstrated that a strong antiferromagnetic spin-exchange interaction is operating between copper(II) and nickel(II) or cobalt(II) ions.



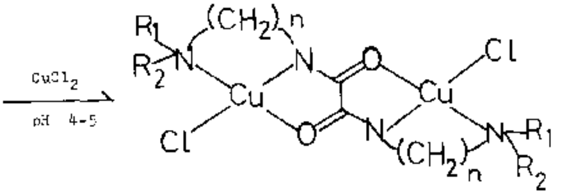
50–52

n	M(II)	μ_{eff} (BM) [a]	No.
2	Ni	3.49	**50**
3	Ni	4.11	**51**
3	Co	5.11	**52**

---

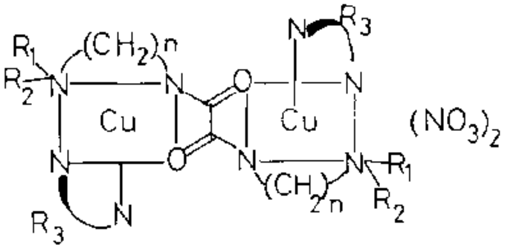
[a] Moment per molecule.

The ligands **13**, **14** and **15** (any R_1, R_2) gave complexes **53–65**, **93–97** and **122–125** in which the ligands adopt a *trans* configuration. The cause of such behaviour is due to the bulk of the second ligands or the bulk of R_1, R_2 [10]. The structures of **57** and **59** (Cl in **53–60** is replaced by SCN^-, CN^-, SO_4^{2-} and imidazole) were demonstrated by means of potentiometric and spectrophotometric methods [19], and structure **59** (X = SCN) was confirmed by X-ray analysis [20].



53–60

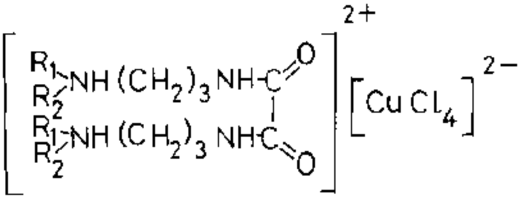
R_1	R_2	n	μ_{eff} (BM)	No.
H	H	3	1.08	**53**
H	CH_3	3	1.17	**54**
CH_3	CH_3	3	1.23	**55**
C_2H_5	C_2H_5	3	1.07	**56**
H	H	2	0.89	**57**
H	CH_3	2	0.91	**58**
CH_3	CH_3	2	0.93	**59**
C_2H_5	C_2H_5	2	0.78	**60**



61-65

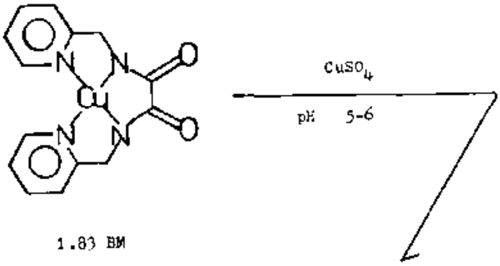
R_1	R_2	R_3	n	μ_{eff} (BM)	No.
H	H	bipy	3	1.31	**61**
H	CH_3	bipy	3	1.32	**62**
H	CH_3	phen	3	1.44	**63**
CH_3	CH_3	phen	3	1.25	**64**
H	H	bipy	2	0.97	**65**

In the presence of excess HCl, the ligand **15** (any R_1. R_2) gave yellow complexes. type **66**, showing normal μ_{eff} values [15].

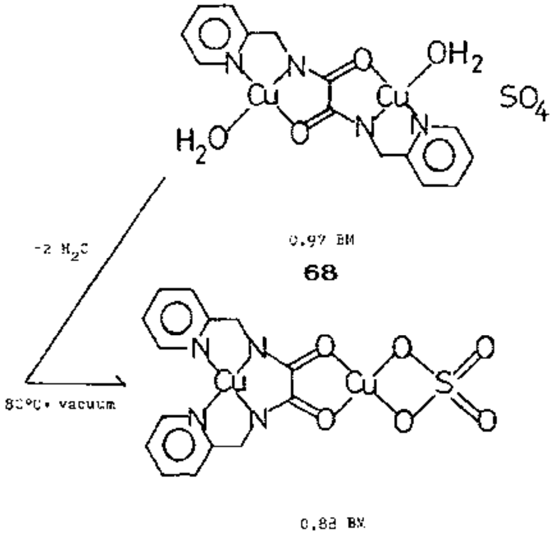


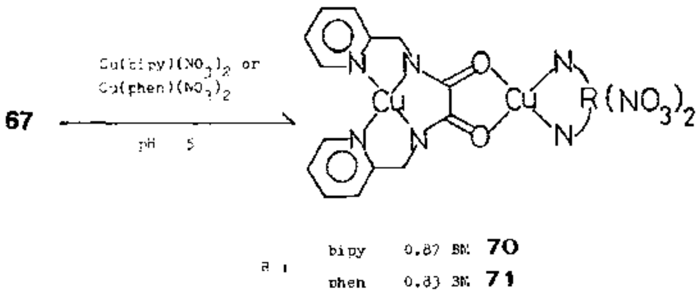
66

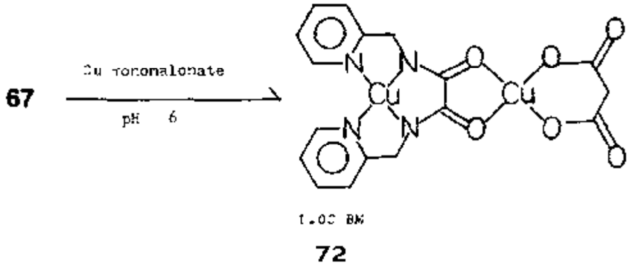
The complex **67** was isolated by reaction of equimolar amounts of ligand **16** and Cu^{2+} at pH 8 [21]. The reactions proceeded further to produce **68–76**. Both **67** and **82** behave as the complex **40** does with change in pH (see Fig. 3).



67 **68**

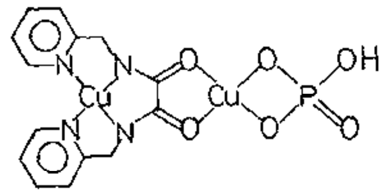






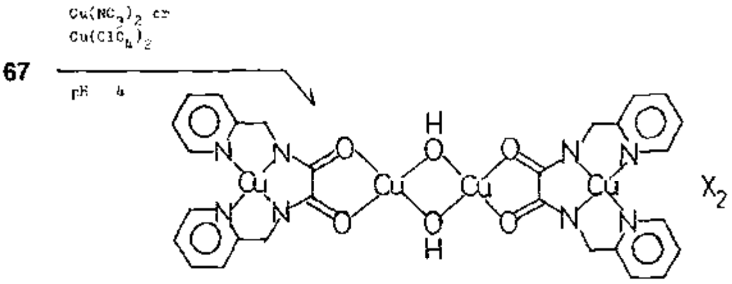
Complex **73** was formed according to the following disproportionation reaction at pH 6 [22]:

$$2\underset{\mathbf{67}}{[\mathrm{CuL}^{2-}]} + \mathrm{H_3PO_4} \rightarrow \left[\underset{\mathbf{73}}{\mathrm{Cu_2L^{2-}(HPO_4^{2-})}} + \underset{\mathbf{16}}{\mathrm{LH_2}}\right]$$

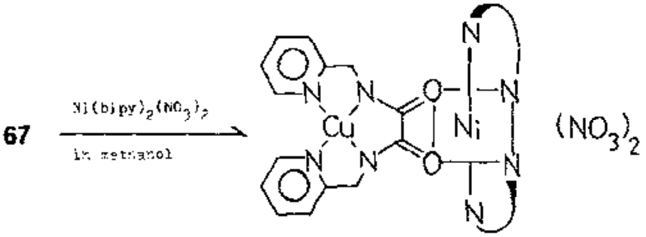


1.11 BM

73



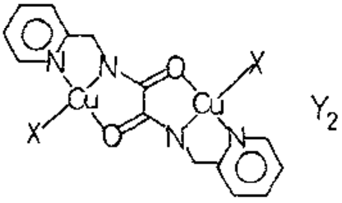
X : NO$_3^-$ 1.02 BM **74** [24]
ClO$_4^-$ 0.95 BM **75** [24]



Existence of magnetic interaction

between Cu and Ni was recognized.[23]

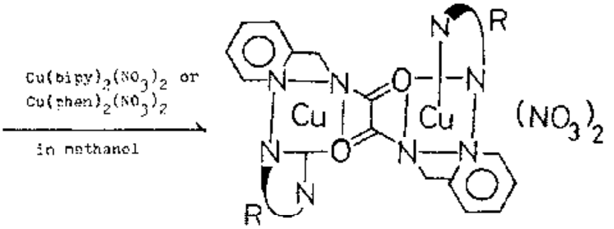
76



77 79

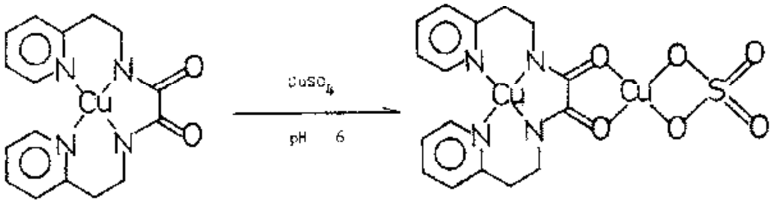
	X	Y	μ_{eff} (BM)	No.
$67 \xrightarrow[\text{pH 5.5–6.0}]{\text{CuCl}_2\text{ or Cu(NO}_3)_2\text{ and KCl}}$	Cl	–	0.81	77
$67 \xrightarrow[\text{pH 3}]{\text{Cu(OH)}_2\text{ and H}_3\text{PO}_4}$	$H_2PO_4^-$	–	1.10	78
$67 \xrightarrow[\text{pH 8–9}]{\text{Cu py}_4\text{(NO}_3)_2}$	py	NO_3^-	0.87	79

67



R : bipy 0.98 BM **80** [23]
phen 0.94 BM **81** [23]

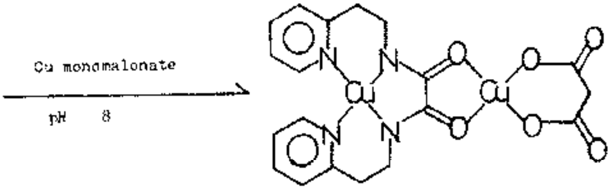
Although species **82** could not be isolated, its existence in an aqueous solution was recognized by a spectrophotometric method. When species **82** coexists with monochelate-ligand coordinated copper(II) complexes, binuclear complexes such as **83–86** (including the moiety of species **82**) could be isolated:



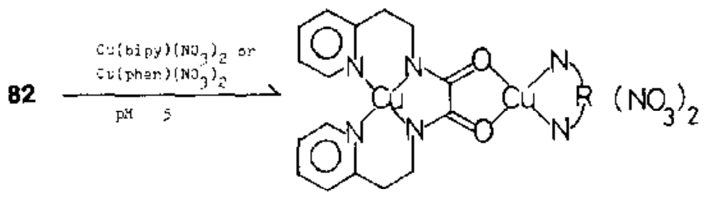
82 [21]

1.15 BM
83 [24]

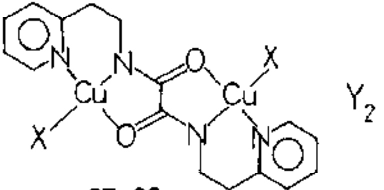
82



1.24 BM **84** [22]

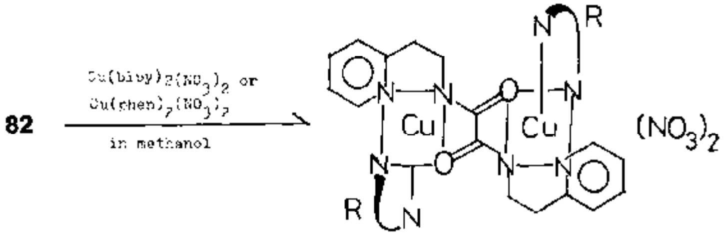


R : bipy 1.12 BM **85** [21]
phen 1.15 BM **86** [23]



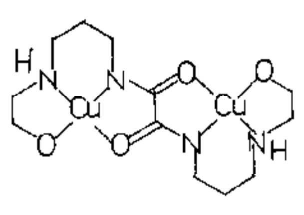
87–90

	X	Y	μ_{eff} (BM)	No.
82 $\xrightarrow[\text{pH 2.5–4.0}]{\text{Cu(OH)}_2\text{ and HClO}_4}$	H_2O	ClO_4^-	1.25	**87**
$\xrightarrow[\text{(vacuum)}]{100\,^\circ\text{C}}$	ClO_4^-	–	1.09	**88**
82 $\xrightarrow[\text{pH 4.5–5.0}]{\text{Cu(NO}_3)_2}$	NO_3^-	–	1.11	**89**
82 $\xrightarrow[\text{pH 5.5–6.0}]{\text{Cu(NO}_3)_2\text{ and KCl}}$	Cl^-	–	1.01	**90**



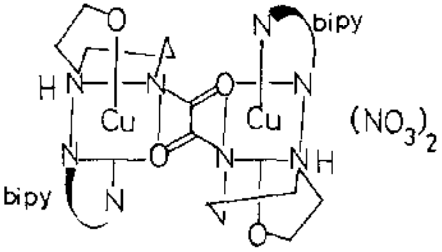
R : bipy 1.44 BM **91** [22]
phen 1.12 BM **92** [22]

Using ligands **18**, **19** and **20**, the complexes **93**–**97** were isolated [25]. The structural dependence on the pH was examined [26].



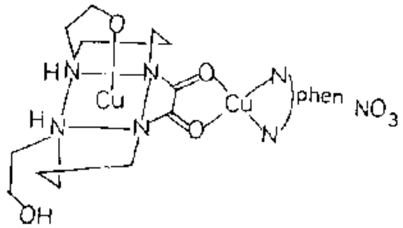
1,50 BM

93



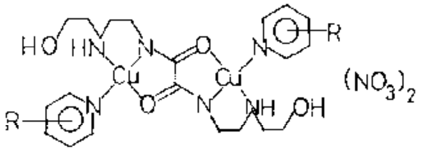
1,47 BM

94



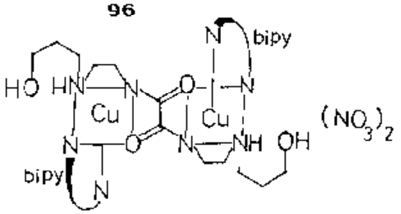
[illegible] BM

95



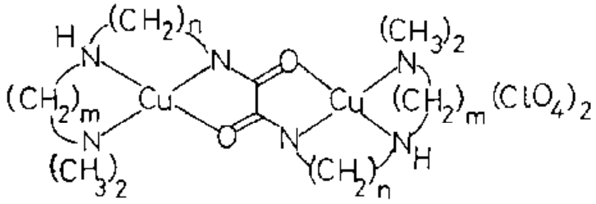
[illegible] BM

96



[illegible] BM

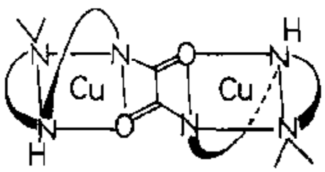
97



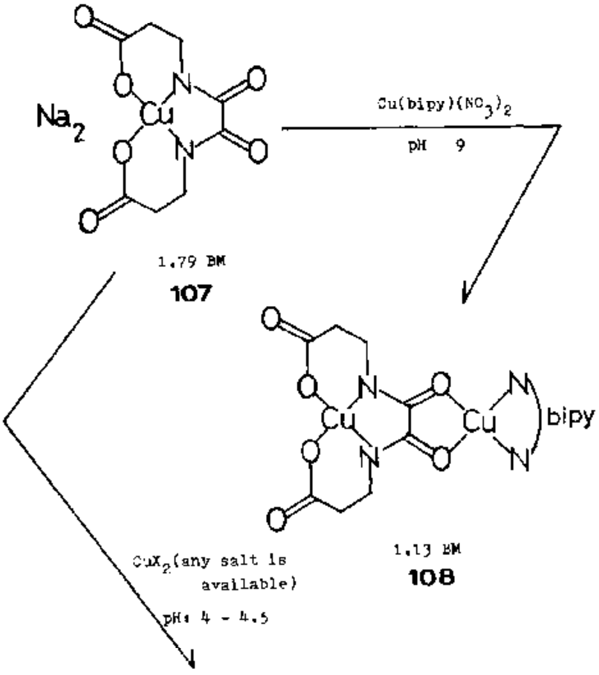
m, *n*	μ_{eff} (BM)	No.
2, 2	0.89	**98**
3, 2	0.92	**99**
2, 3	1.19	**100**
3, 3	1.22	**101**
2, 4	1.25	**102**
3, 4	1.20	**103**
2, 6	1.40	**104**
3, 6	1.15	**105**

The complexes **98–105** were isolated [10]. All the nickel(II) complexes isolated with tetraphenylborate are diamagnetic. The copper(II) complexes were crystallized as chloride and perchlorate, and their μ_{eff} values lie in the range 0.9–1.4 BM. Among them, **104** and **105** were assigned the structure **106** on the basis of the conspicuously lowered ϵ value of the *d–d* band ($\epsilon = 89$ for **105**, but $\epsilon = 140$–200 for the others) which suggests that there is less distortion from square planarity in the ligand field in **105**.

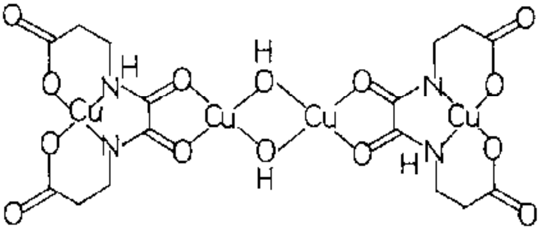
Complex **107** was obtained by reaction of ligand **21** with the cupric salt in equimolar proportions at pH 8, and the complex could be converted to complexes **108** and **109** [27].



106



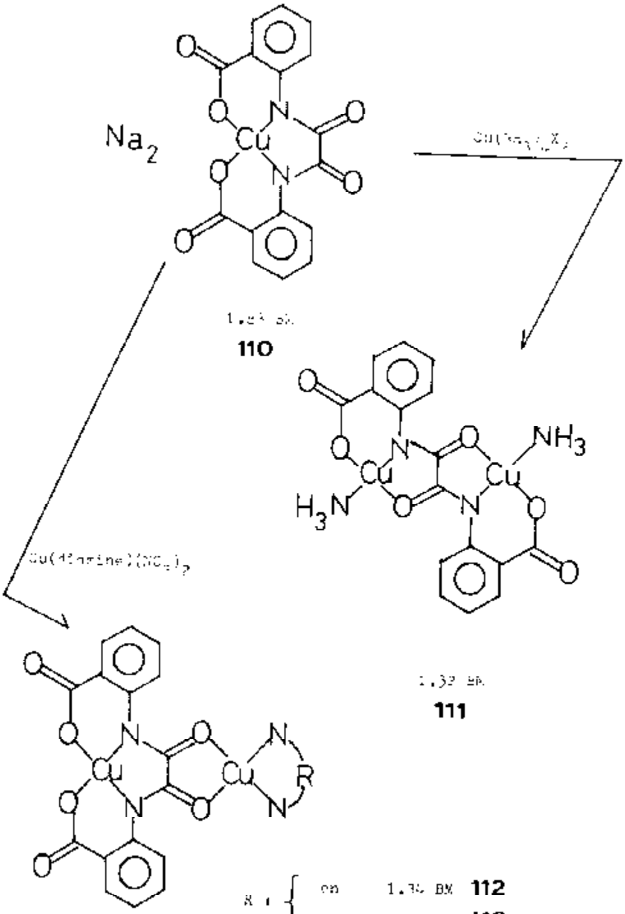
109



1.25 BM

109

Similar complexes, **110–113**, were isolated [28]:



1.83 BM

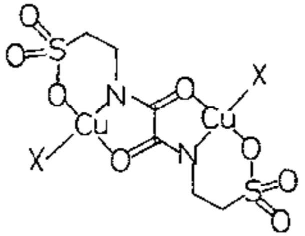
110

1.32 BM

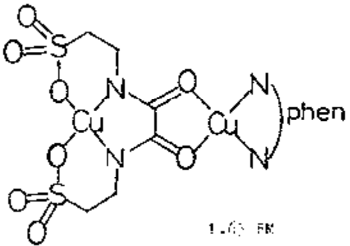
111

R = { en 1.36 BM **112**
bipy 1.26 BM **113**

It has been known for some time that the SO_3^- ion has little coordinating ability. However, the coordination of SO_3^- may take place if the steric condition is favourable for chelate ring formation [29]; complexes **114–118** are successful examples:

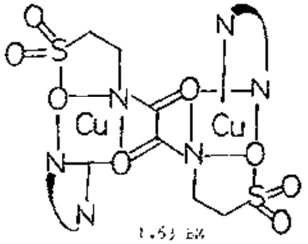


X : imidazole 1.46 BM **114**
pyridine 1.37 BM **115**
γ-picoline 1.23 BM **116**



1.65 BM

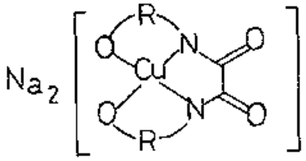
117



1.53 BM

118

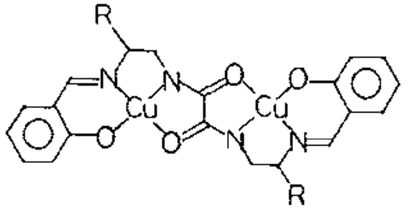
Ligands **25**, **26** and **27** gave complexes **119**–**121** which display their *d–d* band in an unusually high wavenumber region for the Cu · 2N · 2O type [3]. These complexes, as isolated, were invariably contaminated with decomposed products.



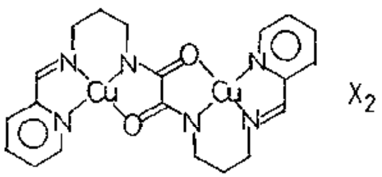
119–121

R	$\nu_{d-d\ \max}$ (kK)	ε	No.
$-CH_2-CH_2$	17.4	100	**119**
$-CH(CH_3)-CH_2-$	17.4	102	**120**
$-CH_2-CH_2-CH_2-$	17.3	79	**121**

Template condensation yielded complexes **122**–**128**, e.g. **122** and **123** were obtained by reaction of 1 mol of complex **57** with 2 mol of salicylaldehyde [30], and **124** and **125** were obtained from 1 mol of complex **53** and 2 mol of pyridine-2-aldehyde [30].

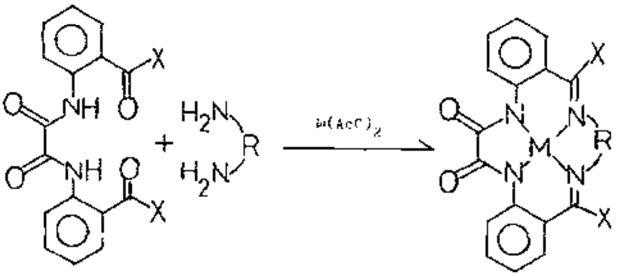


R : H 0.95 BM **122**; CH_3 0.95 BM **123**



X : NO_3^- 1.11 BM **124**; ClO_4^- 1.20 BM **125**

Complexes **127** [31] and **128** can readily be formed from ligand **126** by template condensation. Species **128** and its derivatives were studied by the cryomagnetic method [32].



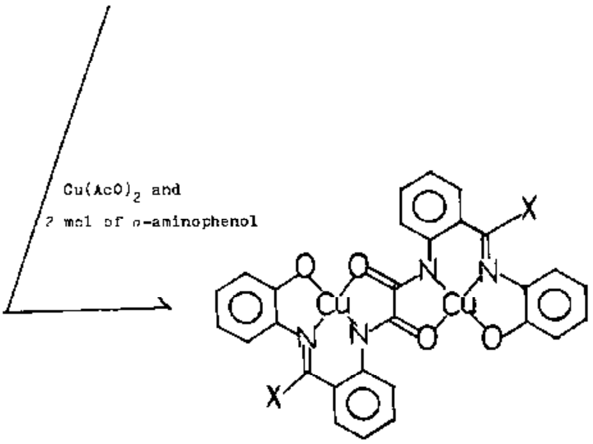
126

127 M : Cu(II), Ni(II), Co(II); R : $-(CH_2)_{2-3}-$ etc.

E. COPPER(II) COMPLEXES WITH COORDINATED *N*-(SUBSTITUENT)OXAMIDES

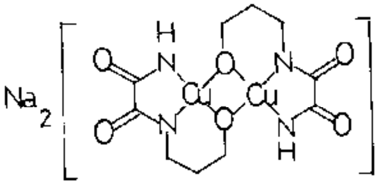
In any mixing ratio of Cu^{2+} and ligand **28**, the complex **129** was always produced in the range between pH 8 and the pH of 1 N NaOH [33]. In the case of the nickel(II) complex, only **130** [33] was obtained, and its structure was confirmed by X-ray analysis [34].

126



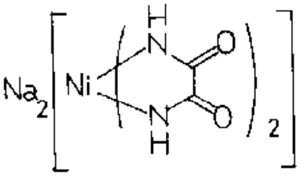
1.72 BM (X=H etc.)

128



0.45 BM

129

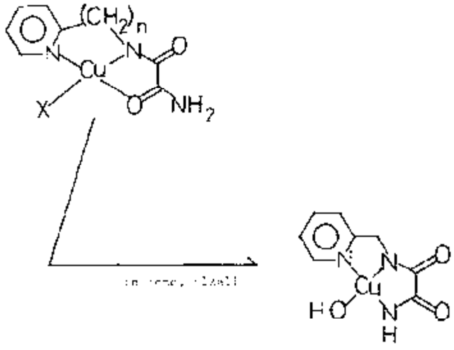


diamagnetic

130

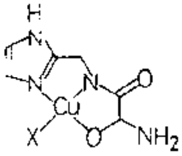
Complexes **131–135** were isolated [33], and species **136** was identified by potentiometric and spectrophotometric methods [35]. The cobalt(II) complex, similar to **131**, was reported to form O_2 adducts [36–38].

Although ligand **31** reacted with Ni^{2+} (pH 10) to afford **137**, reaction with Cu^{2+} gave **138** accompanied by hydrolysis of the end amide groups [33]. However, ligand **30** gave **139** and **140**, no hydrolysis taking place [33]. Species **138** can be converted to **141**, **142** and **143** [39].



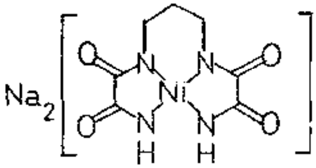
1.74 BM

135



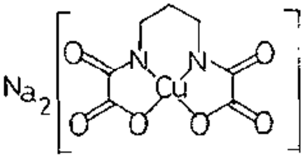
136

n	X	μ_{eff} (BM)	No.
1	Cl^-	1.86	**131**
1	Br^-	1.82	**132**
2	Cl^-	1.85	**133**
2	Br^-	1.78	**134**



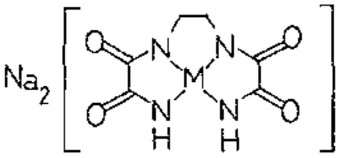
diamagnetic

137

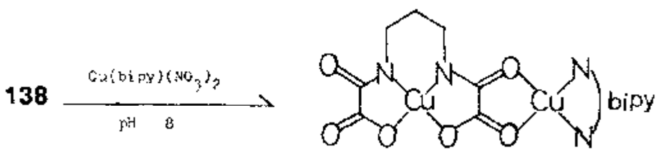


1.85 BM

138

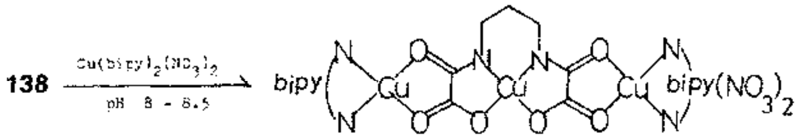


M = Ni(II) diamagnetic **139**
Cu(II) 1.80 BM **140**



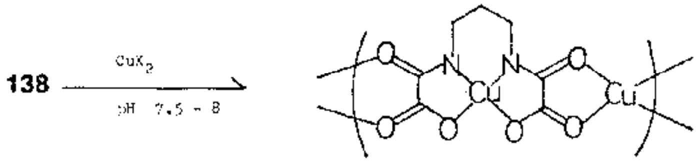
1.30 BM

141



1.33 BM

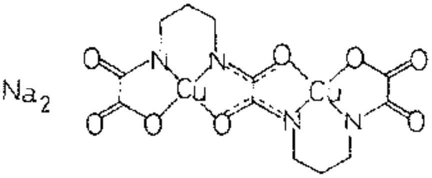
142



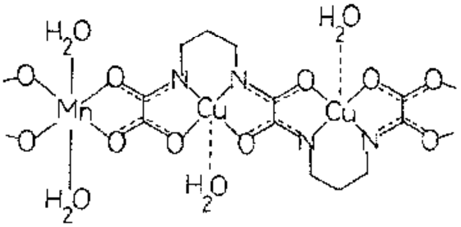
1.26 BM

143

From ligand **32**, bimetallic chains, $Mn \cdot Cu(L^{2-})(H_2O)_3 \cdot 2H_2O$, were isolated and the structure was determined [40]. The related complexes, **144** and **145**, were also reported [40].



144

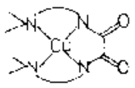


145

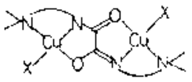
F. COMMON PROPERTIES OF COPPER(II) COMPLEXES WITH OXAMIDES

(i) Ligand-field transitions

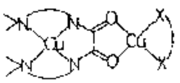
The features of the ligand-field *d–d* bands are classified into the following four types:



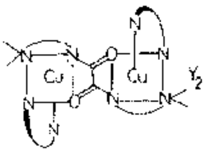
type 1



type 2



type 3



type 4

Type 1. Reflecting the strong planarity of the Cu · 4N-type ligand field, $\nu_{d-d \max}$ appears in an unusually high wavenumber region, higher than that of the corresponding amine complexes.

Type 2. Since both ligand fields of this binuclear complex are equivalent, the *d–d* structure is simple as expected. However, complexes of the Cu · 3N · O type show a red shift from complexes of type 1.

Type 3. Because complexes of this type have two different ligand fields, each producing its own *d–d* band, a broad absorption curve is observed. In addition, a characteristic charge transfer band is superposed on the higher frequency side of the *d–d* band.

Type 4. Both ligand fields within the binuclear complex are equivalent, each having a five-coordinate configuration. The *d–d* band is markedly split owing to a lowering of the ligand-field symmetry [41–44].

In all cases the *d–d* ϵ values at $\nu_{d-d \max}$ for 5–5 or 5–5–5 member fused chelates are always higher than those for the 6–5 or 6–5–6 member species, the ϵ of the former being two or more times as large as that of the latter [14,45]. This suggests that the distortion from square planarity of the former (5–5 or 5–5–5 member species) is larger than that of the latter.

(ii) Charge transfer band

All the binuclear copper(II) complexes with oxamides coordinated as bridging ligands display strong charge transfer bands (near 30 kK, $\epsilon =$

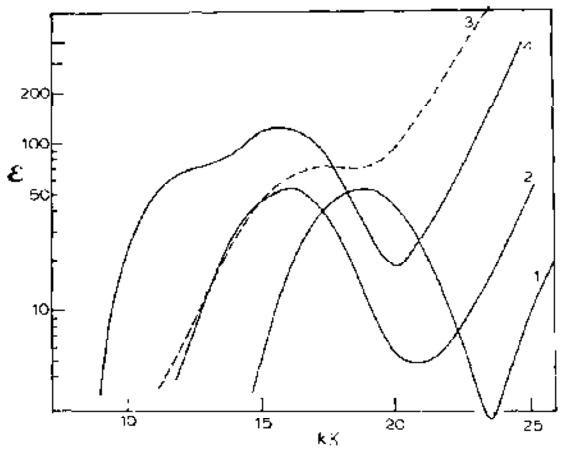


Fig. 4. Features of the $d-d$ band for each type: curve 1, type 1; curve 2, type 2; curve 3, type 3; curve 4, type 4.

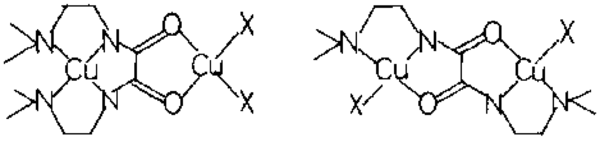
$\epsilon = 1000-1400$) which may be due to the electron spin interaction between the two copper(II) ions through the π-path orbital set up by the oxamide bridge [46]. This requires more detailed study.

(iii) IR spectra

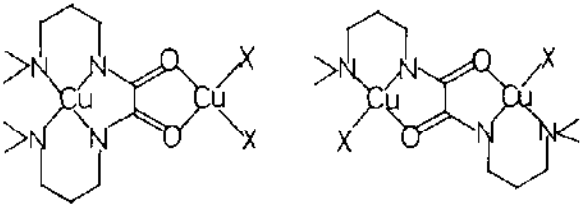
One characteristic IR spectroscopic feature of dimeric copper(II) complexes with a bridging oxamide ligand is observed in their amide I bands. In general, when the deprotonated amide nitrogen is coordinated to the metal ion, its amide I band shifts considerably towards lower wavenumber (40–90 cm^{-1}) [47]. In the case of an oxamide dianion coordinated to two metal ions as a bridging ligand, the amide I band reverts to near its original position (in the protonated species) [22]. Although the amide I band is due to a composite N–C=O vibration, it can essentially be seen as $\nu_{C=O}$. Therefore it is likely that the bond order of C=O in a binuclear complex is higher than that in a mononuclear complex such as **40** and **67**. This experimental fact can be used as definite proof for bridging coordination of the oxamide dianion compared with the non-bridging case.

(iv) The relationship between μ_{eff} values and ESR signal intensities in binuclear oxamidodicopper(II) complexes

The μ_{eff} values of dimeric copper (II) complexes presented here can be classified into two categories, group **a** and **b**. For any kind of X, the μ_{eff}



group **a**



group **b**

values for complexes in group **a** lie in the range 0.8–1.0 BM, whereas the values for complexes in group **b** lie in the range 1.1–1.3 BM [16,17,22–24]. Thus the magnetic interaction between two Cu^{2+} in group **a** complexes is stronger than that in group **b** complexes.

It is known that the relative stabilities of copper(II) complexes consisting of 6–5–6, 5–6–5 or 6–5 member fused chelates (including group **b**) are always higher than those of the 5–5–5 or 5–5 complexes (including group **a**) [48–50]. These results were obtained by a spectrophotometric method using equimolar mixtures of Cu^{2+}, ligand (sample) and ligand (standard). In other words, the lower relative stability at each ligand field in the binuclear oxamido copper(II) complex makes the magnetic interaction through the oxamide moiety stronger.

Nakano et al. made a quantitative measurement of the ESR signal intensities applying the two-step integral method with a multimode resonator cavity, and applied it to the group **a** and **b** binuclear complexes [51]. The ESR signal intensities thus obtained are proportional to the μ_{eff} values without any inverse point. Thus the nature of the chelate ring, the magnetic moment and the ESR signal intensities, are all internally consistent. The higher the relative stability of each binuclear oxamido complex (consisting of 6–5 or 6–5–6 members), the less extensive is the delocalization of the π electron on the amide bridge. In other words, decreasing the stability of each ligand field in an oxamido dimer molecule is advantageous for setting up the π path.

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