Reaction of Some Aliphatic Diamines with Four-co-ordinated Unsymmetrical Ketoenamine Copper(II) and Nickel(II) Complexes

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The interaction between copper(II) and nickel(II) complexes of 3-acetyl-, 3-benzoyl-, and 3-ethoxycarbonyl-9-methyl-5,8-diazadodeca-3,9-diene-2,11-dione and some aliphatic diamines has been investigated. The copper and nickel chelates when refluxed in neat 1,2-diaminoethane formed complexes with 14-membered tetra-aza macrocycles, whereas under similar conditions the nickel chelates reacted with 1,3-diaminopropane forming acyclic 10-substituted (15-amino-4,11-dimethyl-5,8,12-triazapentadeca-3,9,11-trien-2-onato)nickel(II) derivatives instead of the expected corrin derivatives. The latter products may be considered as precursors to polynuclear species because of the presence of a free unco-ordinated primary amino-group in the molecule.

The increasing interest in tetra-aza macrocyclic metal complexes as model compounds for active sites in enzymes comprising corrin or porphyrin moieties has resulted in various preparative routes to such compounds. One synthetic approach is the template condensation of N_2O_2 quadridentate ketoenamine metal complexes with diamines (Scheme). The reactivity of complexes (**1**) depended grossly on the nature of the R^2 substituent. The ring closure proceeded smoothly in the presence of excess of diamine only when R^2 was XCO– (X = alkyl, aryl, or alkoxy).[1–3] In other cases, particularly when R^2 = H or alkyl, the condensation did not occur[2,3] even under the most forcing conditions. For example, refluxing of [**1**; M = Ni, R = $(CH_2)_2$, $R^1 = R^3 = CH_3$, R^2 = H] in neat 1,2-diaminoethane for 2 d yielded no trace of the corresponding compound (**2**).[4] The preparation of complexes (**2**) with R^2 = H, alkyl, or aryl required different non-template procedures.[4,5]

Funcke and Melson[6] studied the rate of interchange between 'co-ordinated' and 'unco-ordinated' acetyl groups present in the nickel complex [**1**; M = Ni, R = $(CH_2)_2$, R^1 = H, R^2 = $COCH_3$, R^3 = CH_3]. Based upon calculated lifetimes of particular configurations of that complex, they suggested that the carbon atom of the co-ordinated acetyl group is the preferred site for nucleophilic attack by an amine.

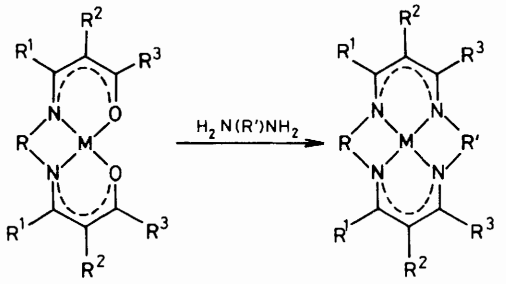
In the course of a study on metal complexes with unsymmetrical quadridentate Schiff bases we prepared the copper and nickel chelates (**3**) and (**4**).[7] These compounds comprise only one –COX substituent in the R^2 (*meso*) position so that nucleophilic attack on one of the co-ordinated carbonyl groups would be favoured. It seemed of interest to study the effect of a single *meso* substituent and the nature of the diamine on the ring-closure process. This paper deals with the reactions of complexes (**3**) and (**4**) with 1,2-diaminoethane and 1,3-diaminopropane.

Results and Discussion

The condensation products of complexes (**3**) and (**4**) with 1,2-diaminoethane are crystalline solids with well defined stoicheiometry and sharp melting points (Table 1). Their analytical and physical data show that they are all metal complexes of a 14-membered tetra-aza macrocyclic ligand, (**5**) and (**6**). On the other hand when complexes (**3**) and (**4**) are treated with 1,3-diaminopropane no cyclisation is observed and the reaction products of (**4**) possess properties consistent with an acyclic structure (**7**).

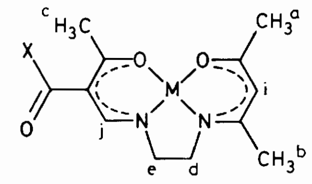
As has been already mentioned, the first step in the reaction between complexes (**3**) and (**4**) and a diamine is nucleophilic attack of a primary amino-group on the carbon atom of the co-ordinated carbonyl group situated in the vicinity of the COX substituent.[2,6] We consider that subsequent closure of the 14-membered macrocyclic ring, occurring only in the 1,2-diaminoethane system, is favoured mainly by the high thermodynamic stability of co-ordinated macrocycles of this size. Formation of a 15-membered ring in the 1,3-diaminopropane system may be hindered by the expected strain in the trimethylene chain.[8] Calorimetric studies have recently shown[9] that copper and nickel complexes with 14-membered macrocycles of the 6-5-6-5 type, generated by fusion of four alternating six- and five-membered chelate rings, are much more stable than their 15-membered 6-5-6-6 analogues.

In the mass spectra of products (**5**)—(**7**) (Tables 2 and 3) the molecular ion is the base peak. Complexes (**5**) and (**6**) exhibit few weak fragmentation ions, formed by the loss of side groups from the macrocyclic ring. On the other hand, the spectra of (**7**) exhibit a number of prominent peaks which may be divided into three groups arising from three main fragmentation pathways. The first group of peaks, similarly to those of



(1) (2)

Scheme.



M = Cu	X	M = Ni
(3a)	CH_3	(4a)
(3b)	C_6H_5	(4b)
(3c)	OC_2H_5	(4c)

Table 1. Analytical and physical data of the complexes

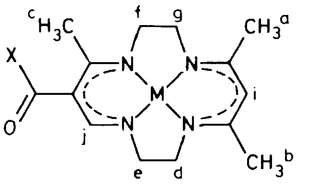
Compound	M.p. (°C)	Yield (%)	Analysis (%)* C	H	N
(5a)	168	61	53.3 (53.3)	6.55 (6.55)	16.35 (16.6)
(5b)	146	65	60.05 (60.05)	6.00 (6.05)	13.8 (14.0)
(5c)	113	53	52.1 (52.25)	6.45 (6.55)	15.0 (15.25)
(6a)	191	61	54.05 (54.1)	6.65 (6.60)	16.55 (16.8)
(6b)	172	65	61.0 (60.8)	6.15 (6.10)	13.95 (14.2)
(6c)	144	72	52.95 (52.95)	6.60 (6.65)	15.3 (15.45)
(7a)	139	78	52.5 (52.65)	7.10 (7.20)	15.3 (15.35)
(7b)	153	52	58.85 (59.05)	6.60 (6.60)	12.85 (13.1)
(7c)	111	68	51.45 (51.65)	7.10 (7.15)	14.0 (14.2)

* Calculated values are given in parentheses.

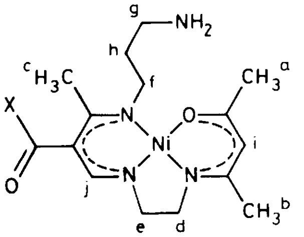
Table 2. Monoisotopic mass spectra* of complexes (**5**) and (**6**)

(5a)	**(5b)**	**(5c)**	**(6a)**	**(6b)**	**(6c)**	Assignment
337(100)	399(100)	367(100)	332(100)	394(100)	362(100)	$P^{\bullet +}$
322(4)		322(9)	317(40)	317(7)	317(7)	$[P - \mathrm{X}^{\bullet}]^+$
		294(2)	289(11)	289(3)	289(4)	$[P - \mathrm{X\dot{C}O}]^+$
43(3)	105(24)		43(18)	105(2)		$[\mathrm{XCO}]^+$

* Values of *m*/*e* are given for the most abundant isotopes, with relative abundances in parentheses; *P* denotes a parent (molecular) ion peak.



M = Cu	X	M = Ni
(5a)	CH_3	**(6a)**
(5b)	C_6H_5	**(6b)**
(5c)	OC_2H_5	**(6c)**



X
(7a) CH_3
(7b) C_6H_5
(7c) OC_2H_5

complexes (**5**) and (**6**), arises from loss of the side substituents from the molecular ion. The second set consists of peaks corresponding to fissions within the ethylene bridge. Such a mode of fragmentation has been observed previously for other symmetrical[10] and unsymmetrical[11] quadridentate Schiff-base complexes. The fragmentation of the aminopropyl group gives rise to the third sequence of ions separated by *m*/*e* 14. This pattern of peaks, characteristic of unbranched aliphatic primary amines, provides direct proof of the structure (**7**) with a pendant aminopropyl chain.

Proton n.m.r. spectral data for the diamagnetic nickel chelates are given in Table 4. The spectra of complexes (**6**) and (**7**) bear general resemblance to those of (**4**), nevertheless some differences are evident. Methylene groups attached to the nitrogen atoms in complexes (**6**) and (**7**) give rise to a complex pattern of doubled intensity in comparison with that of the corresponding (**4**). The signal can be resolved into two resonances only in the case of (**6b**) and may be assigned to two ethylene bridges. In the case of complexes (**7**) two additional resonances are observed: a singlet due to the primary amino-group and a featureless multiplet due to the methylene group h. A singlet due to the methine proton i of complexes (**6**) is shifted upfield by about 0.3 p.p.m. in comparison with that of corresponding (**4**) due to the replacement of the neighbouring carbonyl group by the less electronegative C=N group. Moreover, the overlapping resonances of methyl groups a,b of complexes (**4**) are observed in the spectra of corresponding (**7**) as two separate singlets shifted slightly upfield. This shift may be explained by steric interaction of the free aminopropyl group causing slight distortion of the complex from a planar structure and thus changing the magnetic environment near those methyl groups. Presumably the upfield shift of the resonance of methine proton j on going from planar (**6**) to slightly twisted (**7**) is caused by a similar effect.

In the vibrational spectra of all complexes (**7**) a slightly broadened band of medium intensity corresponding to stretching vibrations of the primary amino-group is observed at 3 280 cm^{-1}. The position of this band is the same as for free 1,3-diaminopropane, indicating[12] that the primary amino-group in complexes (**7**) is not involved in co-ordination to nickel.

Electronic spectral data (Table 5) are consistent with a planar structure for all the complexes. The *d*–*d* bands of complexes (**5**) are shifted by about 50 nm towards the red in comparison with complexes (**3**),[7] the corresponding change of colour being from purple to green. On the other hand, complexes (**6**) and (**7**) exhibit a *d*–*d* band in a similar region to that of (**4**), *i.e.* 518—534 nm, and show no absorption up to 1 600 nm. This is particularly informative in the case of complexes (**7**) because it confirms that nickel does not exceed a co-ordination number of four, that is the complexes are planar and the primary amino-group is not involved in co-ordination. This conclusion is in accord with earlier reports[8] that planar nickel complexes with quadridentate

Table 3. Monoisotopic mass spectra of complexes (**7**)

(**7a**)	(**7b**)	(**7c**)	Assignment
364(100)	426(100)	394(100)	$P^{\bullet +}$
349(26)	349(8)		$[P - X^{\bullet}]^+$
	321(5)	321(9)	$[P - X\dot{C}O]^+$
253(36)	315(18)	283(26)	 $NH_2CH_2CH_2CH_2NC(CH_3)C(COX)CH\overset{+}{N}{=}CH_2$ Ni
169(36)	169(9)	169(20)	 $CH_3C(O)CHC(CH_3)\overset{+}{N}{=}CH_2$ Ni
334(87)	396(28)	364(32)	$[P\text{–}NH_2CH_2^{\bullet}]^+$
320(88)	382(51)	350(65)	$[P\text{–}NH_2CH_2CH_2^{\bullet}]^+$
306(77)	368(15)	336(17)	$[P\text{–}NH_2CH_2CH_2CH_2^{\bullet}]^+$ and $[P\text{–}Ni]^+$
292(63)	354(7)	322(17)	$[P\text{–}NH_2CH_2CH_2CHNH]^{\bullet +}$
58(9)	58(6)	58(9)	$NH_2CH_2CH_2CH_2^+$ and Ni^+
44(26)	44(9)	44(33)	$NH_2CH_2CH_2^+$
30(21)	30(22)	30(28)	$NH_2CH_2^+$

Table 4. Proton n.m.r. spectra of nickel complexes *

	Methyl			Methylene				Methine		Aromatic		
Compound	a,b	c	X	d,e	f,g	h†	X	i	j	X‡	X†·§	Primary amine
(**4a**)	1.94 (s)	2.43 (s)	2.27 (s)	3.04 (t), 3.26 (t)				4.98 (s)	7.44 (s)			
(**6a**)	1.94 (s)	2.37 (s)	2.25 (s)	3.10—3.45 (m)				4.68 (s)	7.65 (s)			
(**7a**)	1.78 (s), 1.89 (s)	2.36 (s)	2.20 (s)	2.90—3.80 (m)		1.98 (m)		4.95 (s)	7.25 (s)			¶
(**4b**)	1.94 (s)	2.19 (s)		3.03 (t), 3.13 (t)				4.99 (s)	7.17 (s)	7.57 (dd)	7.41 (m)	
(**6b**)	1.93 (s), 1.95 (s)	2.31 (s)		3.25 (t), 3.35 (t)	3.12 (s)			4.68 (s)	7.33 (s)	7.53 (dd)	7.40 (m)	
(**7b**)	1.81 (s), 1.87 (s)	2.20 (s)		2.37—3.35 (m)		1.97 (m)		4.95 (s)	7.13 (s)	7.56 (dd)	7.35 (m)	1.43 (br)
(**4c**)	1.96 (s)	2.43 (s)	1.32 (t)	3.03 (t), 3.24 (t)			4.18 (q)	4.98 (s)	7.56 (s)			
(**6c**)	1.94 (s)	2.39 (s)	1.28 (t)	3.07—3.40 (m)			4.15 (q)	4.63 (s)	7.83 (s)			
(**7c**)	1.80 (s), 1.87 (s)	2.40 (s)	1.27 (t)	2.89—3.45 (m)		1.97 (m)	4.15 (q)	4.91 (s)	7.42 (s)			1.27 ‖

* 220-MHz Spectra (δ/p.p.m.) in $CDCl_3$ solution with $SiMe_4$ as internal reference. s = Singlet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, br = broadened band. † Position of the most intense peak of multiplet. ‡ *ortho*. § *Meta* and *para*. ¶ Signal obscured by overlapping resonances. ‖ Signal partially overlapped by triplet of methyl group in X.

Table 5. Electronic spectra[a] of the metal complexes[b]

Compound	$\lambda_{max.}$/nm
(**5a**)	298 (4.34), 327 (4.28), 590 (2.23)
(**5b**)	330 (4.32), 590 (2.29)
(**5c**)	283 (4.42), 328 (4.23), 586 (2.19)
(**6a**)	257(4.09), 282(4.14), 331(4.19), 530(2.45)
(**6b**)	277 (4.27), 368 (4.09), 532 (2.56)
(**6c**)	292 (4.36), 378 (3.77), 534 (2.38)
(**7a**)	258 (4.09), 318 (4.25), 518 (2.54)
(**7b**)	234 (4.41), 345 (4.16), 526 (2.63)
(**7c**)	239(4.32), 274(4.28), 347(3.75), 528(2.47)

[a] Values of log $\varepsilon_{max.}$ are given in parentheses. [b] For solutions (2×10^{-3} mol dm^{-3}) in acetonitrile (nickel complexes) or methanol (copper complexes).

Schiff bases generated by fusion of three 6-5-6-membered chelate rings show no tendency to form adducts with ligands having strong co-ordination properties such as pyridine.

The presence of the free amino-group in complexes (**7**) creates the possibility of the condensation of this group with a variety of other compounds comprising carbonyl groups. Thus these complexes may be regarded as potential precursors in the synthesis of unsymmetrical bi- and poly-nuclear species.

Experimental

Carbon, hydrogen, and nitrogen contents were determined on a Carlo Erba Elemental Analyser MOD 1106. Mass spectra were recorded on a MS 30 A.E.I. Scientific Apparatus spectrometer at 70 eV (*ca.* 1.1×10^{-17} J). Proton n.m.r. spectra were obtained on a Perkin-Elmer R-34 220 MHz spectrometer, u.v. and visible absorption spectra on a Perkin-Elmer UV-VIS 402 spectrometer, and i.r. spectra on a Specord 71 spectrometer using hexachlorobutadiene mulls.

Reagents.—1,2-Diaminoethane and 1,3-diaminopropane (Fluka) were dried over potassium hydroxide and distilled. The preparation of the copper(II) and nickel(II) complexes (**3**) and (**4**) respectively was described earlier.[7]

General Preparation of Macrocyclic Complexes (**5**) *and* (**6**).—One of the complexes (**3**) or (**4**) (0.5 g) was dissolved in 1,2-diaminoethane (5 cm^3) and refluxed for 2 h. The resulting solution was evaporated under reduced pressure to remove the excess of amine and the residue was treated with ice-cold water (10 cm^3), whereupon a coloured solid precipitated. This was filtered off, washed several times with cold water, dried, and recrystallised from methanol–acetonitrile to give green (**5**) and red (**6**). Analytical data and yields of the complexes are listed in Table 1.

General Preparation of Acyclic Nickel Complexes (**7**).—This followed a similar procedure to that above except that 1,3-diaminopropane was used instead of 1,2-diaminoethane. The red-brown complexes were recrystallised from methanol–di-isopropyl ether. Analytical data and yields of the complexes are given in Table 1. The copper complexes (**3**) when refluxed in 1,3-diaminopropane yielded no solid products.

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