Bromination Reactions Involving Nickel and Copper Complexes of Schiff-base Derivatives of Acetylacetone

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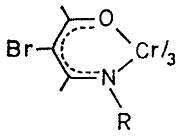
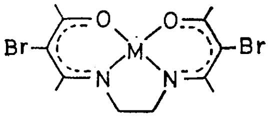
Bromination, in acetonitrile or chloroform of nickel(II) and copper(II) complexes of 5,8-diazadodeca-4,8-diene-2,11-dione and the nickel(II) complex of 6-methyl-5,8-diazadodeca-4,8-diene-2,11-dione has been studied. The products obtained contain two bromine atoms per molecule of complex. The ligand can be brominated with *N*-bromosuccinimide in the absence of a metal ion and the product reacts with nickel(II) or copper(II) ions to yield identical complexes to those obtained when the reaction is performed on the complexes of the corresponding non-brominated ligand.

BROMINATION occurs at the 3-position of the ligand in a range of acetylacetonatometal complexes.[1] The electron density at the central carbon of the chelate ring is an important factor in the success or failure of these electrophilic substitutions. This density has been shown to be dependent on both the type of metal ion as well as the nature of any other ligands present in the complex.[2]

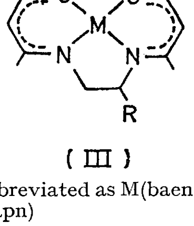
There have been a few isolated investigations on systems in which one of the oxygen atoms in the acetylacetonate rings is replaced by another heteroatom. For example, the chromium(III) complexes of α-β-unsaturated-β-aminoketones have been prepared[3] and brominated[4] to yield products of type (I).


(I)


(II)

No comprehensive investigation of reactions involving quadridentate ligand complexes derived from acetylacetone has been performed. However it has been briefly reported[5] that (5,8-diazadodeca-4,8-diene-2,11-dione)copper(II) undergoes bromination on reaction with *N*-bromosuccinimide in chloroform but, apart from elemental analysis, no evidence was given to support the formulation of the product as structure (II; M = Cu). In addition, the brominated product was isolated in quite small yield.

An investigation of bromination reactions involving the complexes (III; M = Ni, R = H or Me and M = Cu, R = H) is reported here.

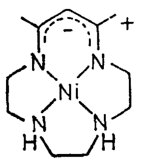

(III)

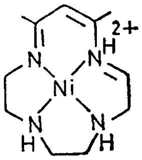
When R = H, (III) abbreviated as M(baen); when R = Me, (III) abbreviated as M(bapn)

RESULTS AND DISCUSSION

Reactions in a 2 : 1 stoicheiometric ratio of *N*-bromosuccinimide with (III; M = Ni, R = H and Me; M = Cu, R = H) in acetonitrile leads, in each case, to isolation of a product which contains two bromine atoms per molecule of complex (Table 1). All the products, which are acid-labile, were obtained in good yield and this is probably a consequence of the fact that strongly acidic by-products are not generated during the course of the reaction. In contrast, although substitution of bromine for *N*-bromosuccinimide in the reaction with Ni(baen) gives the same brominated product, Ni(baenBr_2), the reaction conditions must be carefully controlled and the yield is much reduced. In this case the reduced yield of required product is a consequence of acid degradation as we have observed that a considerable amount of ethylenediamine dihydrobromide as well as lesser amounts of other products can be isolated from the reaction solution.

It is interesting to compare the behaviour of bromine with Ni(baen) in acetonitrile with its behaviour with the nickel complex (IV) in the same solvent.[6] Although the macrocyclic ligand in this complex is derived from acetylacetone, electrophilic bromination of the centre carbon of the acetylacetone portion of the ligand does not occur. Instead oxidative dehydrogenation is observed such that a new product (V) containing increased conjugation is produced. Since very little is as yet known about the role of the metal ion in oxidations of the latter type[7] it is inappropriate to speculate about the reasons for the differing behaviour of bromine with these two classes of nickel complex.


(IV)


(V)

The complex Ni(baenBr_2) is a typical product of the bromination reactions. Like Ni(baen), this compound is diamagnetic and it shows a single absorption at 580 nm in its visible reflectance spectrum. Although the assign-

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[1] J. P. Collman, *Angew. Chem. Internat. Edn.*, 1965, **4**, 132.

[2] J. P. Collman, 'Advances in Chemistry' Series, No. 37, American Chemical Society, Washington, D.C., 1963, p. 78.

[3] R. P. Dryden and A. Winston, *J. Phys. Chem.*, 1958, **62**, 635.

[4] J. P. Collman and E. T. Kittleman, *Inorg. Chem.*, 1962, **1**, 499.

[5] R. W. Kluiber, *J. Amer. Chem. Soc.*, 1960, **82**, 4839.

[6] C. J. Hipp, L. F. Lindoy, and D. H. Busch, *Inorg. Chem.*, 1972, **11**, 1988.

[7] L. F. Lindoy, *Quart. Rev.*, 1971, 379.

ment of the transition responsible for this absorption is somewhat uncertain, its presence is nevertheless characteristic of a square-planar geometry. In other related complexes containing a *cis*-NiO_2N_2 planar environment this absorption has been ascribed to the $^1A_1 \longrightarrow {}^1B_1$ transition.[8] The compound is a non-electrolyte in nitromethane and addition of aqueous silver nitrate to an alcohol solution of the complex does not yield a precipitate of silver bromide. These observations indicate that the two bromines are not present in the complex as free or co-ordinated bromide ions and hence confirm that bromination of the organic ligand has occurred.

TABLE 1

Elemental analyses for the brominated products

Product	Colour	Analyses (%) Found C	H	N	Br	Calculated C	H	N	Br	% Yield *
Ni(baenBr_2) [a]	Green	33·2	3·7	6·5	36·5	32·9	3·7	6·4	36·4	72
Ni(baenBr_2) [b]	Green	32·3	3·9	6·4	35·9					30
Ni(baenBr_2) [c]	Green	32·8	3·8	6·2						77
Ni(bapnBr_2) [a]	Green-brown	34·8	4·1	6·4	35·1	34·5	4·0	6·2	35·3	41
Cu(baenBr_2) [a]	Navy blue	32·8	3·7	6·4		32·5	3·6	6·3		46
Cu(baenBr_2) [c]	Navy blue	32·7	3·8	6·4						52
baenBr_2	Pale yellow	37·9	4·8	7·3		37·7	4·8	7·3		79

[a] Prepared by reaction of *N*-bromosuccinimide with the appropriate metal complex. [b] Prepared by reaction of bromine with Ni(baen). [c] Prepared directly from the brominated ligand.

* Before recrystallisation.

TABLE 2

Compound	^{1}H N.m.r. data [a] =CH– (Diketone)	CH_2 or CH (Diamine)	CH_3 (Diketone)	CH_3 (Diamine)	Selected i.r. absorptions [b] C=O and C=C (Stretching modes)	C–H (In-plane bending mode)
baen [c]	5·00	6·58	8·00, 8·08		1580, 1520	1145
baenBr_2 [d]		6·41, 6·44, 6·47	7·63, 7·78		1560	
Ni(baen) [c,d]	5·10	6·93	8·13		1585, 1510	1120
Ni(baenBr_2) [d]		6·81	7·76, 7·80		1545	
Cu(baen)					1575, 1545, 1525	1185
Cu(baenBr_2)					1550	
(bapn) [c]	5·02, 5·04	6·72	8,00, 8·09, 8·12	8·73		
Ni(bapn) [c,d]	5·11, 5·15	6·73,[e] 7·33 [f] (ratio 2 : 1)	8·14 [e]	8·69	1585, 1520, 1510	1205
Ni(bapnBr_2) [d]		6·88,[g] 7·25 [f] (ratio 2 : 1)	7·74 [g]	8·60	1550	

[a] For $CDCl_3$ solutions at 32° C using tetramethylsilane as internal reference; in τ. [b] In cm^{-1}, in paraffin oil mulls. [c] Ref. 10. [d] This work. [e] Major peak of complex multiplet. [f] Doublet (*J* 12 Hz). [g] Complex multiplet.

The positions of bromination have been uniquely determined using n.m.r. and i.r. spectroscopy. A comparison of the n.m.r. spectra of Ni(baen) and Ni(baenBr_2) is given in Table 2. The spectrum of the former compound has been reported previously,[9,10] and contains an absorption due to the hydrogens attached to the centre carbon of the acetylacetone moieties as a singlet at τ 5·00. The n.m.r. spectrum of the brominated complex, while generally similar to the spectrum of Ni(baen), does not contain this singlet and thus Ni(baenBr_2) must have structure (II; M = Ni).

The i.r. spectra of imine derivatives of β-dicarbonyl compounds usually contain two strong bands in the 1600—1500 cm^{-1} region which are associated with the C=O and C=C bond stretches.[4] Substitution of bromine for the hydrogen attached to the central carbon atom of the chelate ring incorporating the β-dicarbonyl fragment yields a product whose i.r. spectrum contains only a single band in this region (*ca.* 1550 cm^{-1}). Similar changes in the i.r. spectra are observed on bromination of a range of metal acetylacetonates.[1,2,11]

We have observed that baen, Ni(baen), and Ni(bapn) all show the two bands expected, whereas the spectrum of each of the corresponding brominated products contains only one band (Table 2). The disappearance of the CH in-plane bending mode at *ca.* 1140 cm^{-1} in the spectra of these compounds is also confirmation that bromination has occurred.

Bromination of baen in the absence of a metal ion also proceeds easily to yield a cream product. The elemental analyses (Table 1), n.m.r. and i.r. spectra (Table 2) of this product indicate that it is the brominated ligand, baenBr_2. Confirmation of the structure of this product is also afforded by the fact that it reacts with nickel acetate to yield green Ni(baenBr_2).

Several attempts to produce a mono-brominated derivative of Ni(baen) by reaction of this complex with

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[8] G. Maki, *J. Chem. Phys.*, 1958, **29**, 1129; R. D. Archer, *Inorg. Chem.*, 1963, **2**, 292; C. M. Kerwin and G. A. Melson, *ibid.*, 1972, **11**, 726.

[9] E. Larsen and K. Schaumburg, *Acta Chem. Scand.*, 1971, **25**, 962.

[10] P. J. McCarthy and A. E. Martell, *Inorg. Chem.*, 1967, **6**, 781.

[11] B. Bock, K. Flatau, H. Junge, M. Kuhr, and H. Musso, *Angew. Chem. Internat. Edn.*, 1971, **10**. 225.

N-bromosuccinimide in less than the required 1 : 1 stoicheiometric ratio were all unsuccessful. Comparative t.l.c. indicated that (apart from the starting complex) Ni(baenBr_2) was the only major metal-containing product formed. Under the conditions of these experiments there is little evidence that the formation of a discrete mono-brominated product is favoured.

N-Bromosuccinimide is known to react by a free radical mechanism in non-polar solvents such as chloroform whereas, in polar solvents, the mechanism can be ionic in nature.[12] Since all the reactions so far discussed were performed in the polar solvent acetonitrile, it was considered worthwhile to attempt the bromination of Ni(baen) in chloroform. The reaction was carried out and, once again, green Ni(baenBr_2) was obtained in high yield. However, although an identical product is obtained in both solvents, this of course does not necessarily imply that the mechanisms of their formation are the same.

Parallel studies have been carried out on the related nickel complex, Ni(bapn), and the results obtained with this complex are in complete accord with those found for Ni(baen). The elemental analyses for the brominated product are listed in Table 1 and the n.m.r. assignments are given in Table 2 together with those for the corresponding starting complex. Because of the unsymmetrical nature of the backbone of the ligand in the latter complex, the hydrogens attached to the centre carbons of the this product does have structure (II) as previously suggested.[5]

A summary of the bromination reactions of baen and its metal complexes is given in the Scheme.

EXPERIMENTAL

The starting ligands and their respective nickel(II) and copper(II) complexes were synthesised according to published methods.[13] The m.p.s of these compounds are as follows: baen 108—109 °C (lit.,[13] 111—111·5 °C), bapn 90—93 °C (lit.,[13] 91 °C), Ni(baen) 196—197 °C (lit.,[13] 195—196 °C), Ni(bapn) 156—157 °C (lit.,[13] 157—157·5 °C), Cu(baen) 135 °C dec. (lit.,[13] 141·5 °C).

All products were dried over P_2O_5 *in vacuo* before analysis.

3,10-*Dibromo*-5,8-*diazadodeca*-4,8-*diene*-2,11-*dione*.—Solid *N*-bromosuccinimide (12·46 g) was added slowly to a stirred solution of 5,8-diazadodeca-4,8-diene-2,11-dione (7·84 g) in acetonitrile (75 ml). An exothermic reaction occurred and a white crystalline *product* (10·5 g) was obtained on stirring the solution for 5 min. Recrystallisation from a chloroform–ethanol mixture gave pale yellow crystals; yield, 7·5 g, m.p. 114 °C (dec.).

(3,10-*Dibromo*-5,8-*diazadodeca*-4,8-*diene*-2,11-*dione*)*nickel*(II).—*Procedure* (1). Bromine (5 ml) in acetonitrile (20 ml) was added dropwise to a stirred solution of (5,8-diazadodeca-4,8-diene-2,11-dione)nickel(II) (10 g) in the same solvent at room temperature until the solution turned green. A green-brown precipitate (4·8 g) formed immediately. This was filtered off and recrystallised from methanol to give green needles of *product*; yield 3·8 g. Further addition of

(1·2 g) was obtained. Recrystallisation from hot methanol gave violet needles; yield 0·3 g.

Procedure (2). *N*-Bromosuccinimide (1·78 g) in acetonitrile (20 ml) was added dropwise to a stirred solution of (5,8-diazadodeca-4,8-diene-2,11-dione)copper(II) (1·48 g) in acetonitrile (50 ml). The solution was stirred for 1 h during which time a reddish purple precipitate (1·2 g) was formed. Recrystallisation from a chloroform–ethanol mixture gave violet needles; yield 0·3 g.

Analyses.—Analyses for carbon, hydrogen, bromine, and nitrogen were performed by Mr. J. Kent of the Microanalytical Laboratory, University of Queensland. N.m.r. spectra were obtained on a Joel Minimar 100 spectrometer. I.r. spectra were recorded on a Perkin-Elmer 337 or a Jasco IRA-1 spectrophotometer.

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