Reactivity of some Coordinated Ligands Containing Sulphur towards Nucleophilic Substitution Reactions. Part I. Reaction of [(substituted 1,2-ethanediylidene)bis(S-methylhydrazinecarbodithioate)NN′SS′(−2)] Nickel(II) and Palladium(II) Chelates with Secondary Amines

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Abstract

The reaction of (I) ($R_1 = R_2$ = Me, Ph and R_1 = Ph, R_2 = H; X = Ni(II) or Pd(II)) with piperidine or morpholine has been studied and different reaction products have been isolated. The isolated products are categorized into: (i) monoadducts (II), (ii) monosubstituted monoadducts (III), (iii) monosubstituted (IV) and (iv) disubstituted (V) complexes. These complexes have been characterized by infrared, electronic and ^{1}H NMR spectra as well as electron impact and field desorption mass spectra.

Introduction

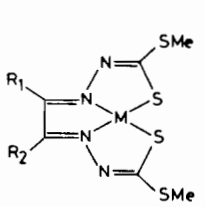
Mono and bisthiosemicarbazones are known to possess a wide spectrum of biological and pharmacological activity [1–7]. In many cases, coordination to transition metal ion enhances their activity [5]. Increase in activity was also observed when the N^4-nitrogen atom was incorporated into a six or seven membered ring such as piperidine, piperazine or azabicyclo 3,2,2-nonane systems [6, 7]. One of the most successful routes for the preparation of N^4-substituted thiosemicarbazides and thiosemicarbazones involves the displacement of the methylmercapto group in S-methylhydrazinecarbodithioate by primary and secondary amines [6, 7]. On the other hand, the displacement of the –SR group from the coordinated thioxanthate ion in binuclear $M_2(S_2CSR)_n(SR)_2$ (M = Ni(II), n = *2*; Co(III) or Fe(III), *n* = 3) chelates by diethylamine to give the corresponding dithiocarbamate ion has also been reported and the reaction products were characterized [8, 9].

These findings, as well as the carcinostatic and carcinolytic activity of α-diketone and α-ketoaldehyde bisthiosemicarbazones [4, 5], developed our interest in investigating the reactivity of nickel(II) and palladium(II) complexes (I) towards secondary amines, e.g. piperidine and morpholine, intending to prepare a series of metal(II) chelates with N^4-mono and disubstituted thiosemicarbazones.

Results and Discussion

The reaction of Ni(II) and Pd(II) complexes (I) ($R_1 = R_2$ = Me, Ph and R_1 = Ph, R_2 = H), hereafter abbreviated respectively as M(Da2SMe), M(Ben2SMe) and M(Phg2SMe) (M = Ni or Pd), with piperidine and morpholine gives different reaction products depending on the central metal ion, the nature of substituents R_1 and R_2, as well as the metal chelate:base molar ratio.

The isolated reaction products, Table I, can be categorized into: (i) monoadducts (II), (ii) monosubstituted monoadducts (III), (iii) monosubstituted (IV) and (iv) disubstituted (V) complexes.



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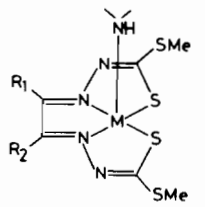

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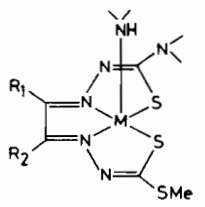

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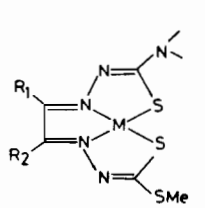

IV

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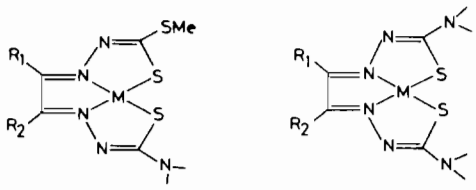
TABLE I. Elemental Analyses of the Isolated Ni(II) and Pd(II) Complexes

Compound	R_1	R_2	N	Analysis[a]		
				N%	S%	M%
(i) Monoadducts (II)						
(1) Ni(Phg2SMe)HPip	Ph	H	HPip	14.5(14.5)	26.8(26.5)	12.4(2.1)
(2) Ni(Phg2SMe)HMorph	Ph	H	HMorph	14.3(14.4)	26.4(26.4)	12.1(12.1)
(ii) Monosubstituted monoadducts (III)						
(3) Ni(PhgSMePip)HPip	Ph	H	Pip	16.2(16.1)	18.0(18.4)	11.6(11.3)
(4) Ni(PhgSMeMorph)HMorph	Ph	H	Morph	16.2(16.0)	18.2(18.3)	11.3(11.2)
(iii) Monosubstituted complexes (IV)						
(5) Ni(DASMePip)	CH_3	CH_3	Pip	18.1(18.0)	24.6(24.8)	15.0(15.1)
(6) Pd(DaSMePip)	CH_3	CH_3	Pip	16.2(16.1)	22.0(22.1)	24.5(24.4)
(7) Ni(DaSMeMorph)	CH_3	CH_3	Morph	18.0(18.0)	24.5(24.7)	15.1(15.1)
(8) Pd(DaSMeMorph)	CH_3	CH_3	Morph	15.7(16.0)	21.3(21.2)	24.1(24.3)
(9) Ni(BenSMeMorph)	Ph	Ph	Morph	13.5(13.6)	18.5(18.7)	11.5(11.4)
(10) Pd(BenSMeMorph)	Ph	Ph	Morph	12.3(12.5)	17.2(17.1)	18.8(18.9)
(11) Ni(PhgSMePip)	Ph	H	Pip	15.8(16.1)	22.0(22.1)	13.5(13.4)
(12) Pd(PhgSMePip)	Ph	H	Pip	14.8(14.5)	19.6(19.9)	21.7(22.0)
(13) Ni(PhgSMeMorph)	Ph	H	Morph	15.9(16.0)	21.9(22.0)	13.2(13.4)
(14) Pd(PhgSMeMorph)	Ph	H	Morph	14.2(14.4)	19.7(19.8)	21.8(22.0)
(iv) Disubstituted complexes (V)						
(15) Ni(Ben2Pip)	Ph	Ph	Pip	15.2(15.3)	11.5(11.7)	10.8(10.7)
(16) Pd(Ben2Pip)	Ph	Ph	Pip	14.3(14.1)	10.7(10.7)	17.6(17.8)
(17) Ni(Ben2Morph)	Ph	Ph	Morph	15.0(15.2)	11.5(11.6)	10.5(10.6)
(18) Pd(Ben2Morph)	Ph	Ph	Morph	13.9(14.0)	10.6(10.7)	17.5(17.7)
(19) Ni(Phg2Pip)	Ph	H	Pip	17.4(17.8)	13.3(13.6)	12.5(12.4)
(20) Ni(Phg2Morph)	Ph	H	Morph	17.5(17.6)	13.3(13.4)	12.5(12.3)
(21) Pd(Phg2Pip)	Ph	H	Pip	16.3(16.1)	12.0(2.3)	20.6(20.4)

[a]Calculated values are in parentheses.



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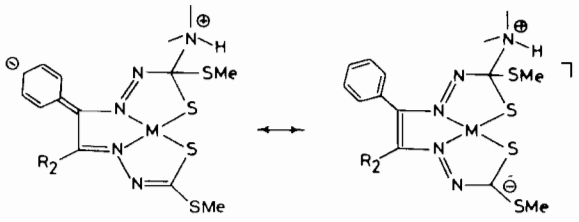

VII VIII

The reaction of Ni(Phg2SMe) with either piperidine or morpholine in ether, using 1:2 molar ratio gave the brown mono-adducts Ni(Phg2SMe)HPip (**1**) and Ni(Phg2SMe)HMorph (**2**) besides the green ether insoluble monosubstituted chelates Ni(PhgSMePip) (**11**) and Ni(PhgSMeMorph) (**13**). Attempts to prepare the corresponding adducts of Ni(Da2SMe) or Ni(Ben2SMe) were unsuccessful and the starting chelates were unchanged. As expected, no adducts were isolated with the analogous Pd(II) complexes due to their reluctance to expand their coordination number.

Furthermore, refluxing M(Da2SMe), M(Ben2SMe) (M = Ni or Pd) and Pd(Phg2SMe) with either piperidine or morpholine in dry benzene in a 1:10 molar ratio for 1 h, also resulted in the formation of the monosubstituted chelates M(DaSMePip) (**5,6**) M(DaSMeMorph) (**7,8**), M(BenSMeMorph) (**9,10**), Pd(PhgSMePip) (**12**) and Pd(PhgSMeMorph) (**14**), respectively, while with Ni(Phg2SMe) the reaction proceeded with the formation of the monosubstituted monoadducts Ni(PhgSMePip)HPip (**3**) and Ni(PhgSMeMorph)HMorph (**4**).

The dipiperidyl complexes M(Ben2Pip) (**15,16**) were prepared from the reaction of M(Ben2SMe)

TABLE II. H NMR Spectra of Nickel(II) and Palladium(II) Complexes in $CDCl_3$

Complex	δ (ppm) (number of protons)[a]							
	$C-CH_3$	$C-SCH_3$	$\beta,\gamma-CH_2-$	$\alpha-CH_2-$	$O-CH_2-$	$-N-CH_2-$	Aromatic	$-CH$
(i) Monoadducts (**II**)								
Ni(Phg2SMe)HPip		2.37(3) 2.47(3)	1.45(6)b	3.10(4)b			7.35(3)m 7.39(2)m	7.15(1)
Ni(Phg2SMe)HMorph		2.35(3) 2.48(3)			2.85(4)m	3.85(4)m	7.30(3)m 7.40(2)m	7.05(1)
(ii) Monosubstituted monoadducts (**III**)								
Ni(PhgSMePip)HPip		2.46(3)	1.45(6)b 1.53(6)b	3.03(4)b 3.60(4)b			7.30(5)m	7.20(1)
Ni(PhgSMeMorph)HMorph		2.44(3)			3.13(4)m 3.20(4)m	3.50(4)m 3.65(4)m	7.35(5)m	
(iii) Monosubstitued complexes (**IV**)								
Ni(DaSMePip)	1.82(3) 2.00(3)	2.50(3)	1.58(6)b	3.68(4)b				
Pd(DaSMePip)	1.98(3) 2.10(3)	2.52(3)	1.58(b)b	3.80(4)b				
Ni(DaSMeMorph)	1.81(3) 2.00(3)	2.48(3)			3.68(4)m	3.71(4)m		
Pd(DaSMeMorph)	2.00(3) 2.18(3)	2.57(3)			3.67(4)m	3.88(4)m		
Ni(BenSMeMorph)		2.45(3)			3.70(4)m	3.71(4)m	7.15(10)m	
Pd(BenSMeMorph)		2.46(3)			3.71(4)m	3.82(4)m	7.15(10)m	
Ni(PhgSMePip)		2.57(3)	1.70(6)b	3.63(2) 4.53(2)			7.37(10)m	7.93(1)
Pd(PhgSMePip)		2.60(3)	1.67(6)b	3.88(4)b			7.32(3)m 7.40(2)m	7.85(1)
Ni(PhgSMeMorph)		2.51(3)			3.70(4)m	3.70(4)m	7.33(10)m	7.82(1)
Pd(PhgSMeMorph)		2.58(3)			3.68(4)m			
(iv) Disubstituted complexes (**V**)								
Ni(Ben2Pip)			1.60(6)b	3.70(4)			7.13(10)m	
Pd(Ben2Pip)			1.65(6)b	3.70(4)			7.11(10)m	
Ni(Ben2Morph)					3.70(4)m	3.70(4)m	7.05(10)m	
Pd(Ben2Morph)					3.70(4)m	3.70(4)m	7.10(10)m	
Ni(Phg2Pip)			1.66(6)b	3.80(4)			7.30(3)m 7.60(2)m	7.10(1)
Pd(Phg2Pip)			1.68(6)b	3.85(4)			7.30(3)m 7.62(2)m	7.13(1)
Ni(Phg2Morph)					3.76(4)m	3.80(4)m	7.30(3)m 7.63(2)m	7.13(1)
Pd(Phg2Morph)					3.70(4)m	3.80(4)m	7.30(3)m 7.63(2)m	7.05(1)

[a]b = broad signal; m = center of a complex multiplet.

(M = Ni or Pd) with a 20-fold excess of piperidine. In the case of M(Da2SMe) and M(Phg2SMe), however, the reaction yielded the monosubstituted complexes M(DaSMePip) (**5**,**6**) and M(PhgSMePip) (**11**, **12**), respectively. The formation of the dipiperidyl complexes M(Phg2Pip) (**19**,**21**) on the other hand, requires at least a 50-fold excess of piperidine.

As morpholine (pK_a 8.33) is less basic than piperidine (pK_a = 11.12), the preparation of dimorpholyl complexes requires a relatively higher base concentration as compared to that used for the corresponding piperidyl complexes. The pure dimorpholyl complexes M(Ben2Morph) (**17**,**18**) have been obtained from the reaction of M(Ben2SMe) (M = Ni or Pd) with morpholine using 1:100 molar ratio. Attempts to prepare either dipiperidyl or dimorpholyl complexes of M(Da2SMe) were unsuccessful and only the monosubstituted complexes were isolated even

TABLE III. Electronic Spectra of Nickel(II) and Palladium Complexes in $CHCl_3$

Complex	Band maxima[a] (log ϵ_{max})						
Ni(Phg2SMe)HPip	255	305	320	400	560		
	(4.5)	(4.3)		(4.3)	(3.1)		
Ni(Phg2SMe)HMorph	255	305	325sh	400	560		
	(4.5)	(4.3)		(4.3)	(3.1)		
Ni(PhgSMePip)HPip	255	305	330sh	400	520sh	720	
	(4.5)	(4.2)		(4.3)		(2.4)	
Ni(PhgSMeMorph)HMorph	255	308	330sh	400	525sh	720	
	(4.5)	(4.3)		(4.2)		(2.4)	
Ni(DaSMePip)	265	340	420	445	530sh	740	
	(4.4)	(4.0)	(4.2)	(4.2)		(2.5)	
Ni(DaSMeMorph)	265	340	420	445	530sh	740	
	(4.4)	(4.0)	(4.2)	(4.2)		(2.4)	
Ni(BenSMePip)	225sh	315	385	445sh	470	560sh	
		(4.3)	(4.1)		(4.3)		
Ni(BenSMeMorph)		315	340sh	395	448sh	480	560sh
		(4.2)		(4.0)		(4.1)	
Ni(PhgSMePip)	295	340	410sh	440	540	600	645
	(4.3)	(3.8)		(3.7)	(3.2)	(3.2)	(3.3)
Ni(PhgSMeMorph)	295	350sh	410sh	440	540sh	600	645
	(4.3)			(3.8)		(3.2)	(3.2)
Ni(Ben2Pip)	225sh	315	390	445sh	470		
		(4.2)	(4.0)		(4.2)		
Ni(Ben2Morph)	225sh	315	398	445sh	470	750b	
		(4.2)	(3.9)		(4.3)		
Ni(Phg2Pip)	266	305	340sh	380	430sh	465	
	(4.5)	(4.3)		(4.1)		(4.2)	
Ni(Phg2Morph)	260	305	340sh	380	430sh	465	
	(4.5)	(4.4)		(4.1)		(4.3)	
Pd(DaSMePip)	265	305	330sh	410	425sh	630	660sh
	(4.2)	(4.3)		(4.2)		(3.2)	
Pd(DaSMeMorph)	265	305	345sh	360	380sh	410sh	
	(4.3)	(4.3)		(4.4)			
Pd(BenSMeMorph)		303	380	430	640sh	690	740sh
		(4.5)		(4.3)		(3.1)	
Pd(PhgSMePip)		300	360	450		670	730sh
		(4.6)		(4.3)		(3.4)	
Pd(PhgSMeMorph)		300	360sh	450		670	730sh
		(4.5)		(4.1)		(3.4)	
Pd(Ben2Pip)		300	370	440	630sh	680	
		(4.4)	(4.1)	(4.3)		(3.2)	
Pd(Ben2Morph)		300	375sh	420sh	440	625	670sh
		(4.4)			(4.3)	(3.5)	
Pd(phg2Pip)			325	400	520sh	620sh	
			(4.4)	(4.3)			
Pd(Phg2Morph)	295	330sh	360	420sh	435	630	680sh
	(4.4)		(4.1)		(4.3)	(4.5)	

[a]sh = shoulder.

when using a very large excess (100–200 equivalents) of the base.

The purity of the isolated complexes were checked by elemental analysis, Table I, field desorption (FD) mass spectra, ^1H NMR spectra, Table II, as well as thin layer chromatographic techniques.

The field desorption mass spectra of the mono-adducts, (**1**) and (**2**), as well as the monosubstituted monoadducts, (**3**) and (**4**), show the corresponding molecular ion peaks at m/e = 483, 485, 520 and 524, respectively, without any sign of decomposition. Their IR spectra exhibit the ν(N–H) of the coordinated piperidine or morpholine at *ca.* 3200 cm^{-1}. These complexes are diamagnetic and show similar solution electronic spectra, (Table III) which are in good agreement with the monomeric low spin five coordinate square pyramidal structure (**II** and **III**).

An inspection of the ^1H NMR spectra, Table II,

of the different types of Ni(II) and Pd(II) complexes reveals that the spectra of the monoaddition products (**1** and **2**) display two different C–SMe singlets at 2.37 and 2.47 ppm due to the presence of different substituents (**II**, R_1 = Ph, R_2 = H). Meanwhile, the monosubstituted monoadducts (**3** and **4**) as well as the monosubstituted complexes (**5–14**) show only one C–SMe singlet at *ca.* 2.50 ppm. The disubstituted complexes (**15–20**), as expected, lack any signals due to –SMe protons. Furthermore, the ^{1}H NMR spectra of the monosubstituted complexes, derived from diacetyl (**IV**, $R_1 = R_2$ = Me, and M = Ni or Pd), display two Me–C=N signals due to molecular asymmetry.

The piperidyl protons of the monosubstituted complexes derived from diacetyl (**IV**, $R_1 = R_2$ = Me and M = Ni or Pd) and benzyl (**IV**, $R_1 = R_2$ = Ph and M = Ni or Pd) appear as two broad signals at *ca.* 1.60 and 3.70 ppm, respectively, due to β,γ–CH_2– and α–CH_2–protons. The spectra of the corresponding monomorpholyl complexes similarly show two close multiplets centered at *ca.* 3.70 and 3.80 ppm, respectively, attributed to N–CH_2– and O–CH_2– protons. However, a different spectral pattern is observed for the monosubstituted nickel(II) complexes derived from phenylglyoxal (**IV**, R_1 = Ph, R_2 = H and M = Ni), Ni(PhgSMePip) and Ni(PhgSMeMorph). Their ^{1}H NMR spectra indicate that the two piperidyl α–CH_2– as well as those of the morpholyl N–CH_2– protons are not equivalent and appear as two signals at *ca.* 3.60, 4.50 and 3.70, 4.60 ppm, respectively. This behaviour suggests a partially restricted rotation around the C–N bond due to extended conjugation with the phenyl group.

It can also be seen from the data given in Table II that the α–CH_2– and N–CH_2– signals of piperidine and morpholine, directly coordinated to Ni(II), are respectively shifted upfield as compared to that of the corresponding piperidyl and morpholyl groups in either mono (**IV**) or disubstituted (**VI**) complexes while the β,γ–CH_2– and O–CH_2– protons appear almost at the same chemical shifts. The observed upfield shift can be related to the shielding effect of the delocalized π-current above the planar NiN_2S_2 rings.

Substitution of one SMe group in symmetric M(Da2SMe) and M(Ben2SMe) (**I**, $R_1 = R_2$ = Me or Ph; M = Ni or Pd) complexes, by either piperidine or morpholine, presumably gives only one reaction product (**IV**, $R_1 = R_2$ = Me or Ph; M = Ni or Pd), while with the asymmetric phenylglyoxal complexes M(Phg2SMe) (**I**, R_1 = Ph, R_2 = H and M = Ni or Pd) two reaction products (**IV**) and/or (**V**) are possible. The ^{1}H NMR spectra and thin layer chromatography of the monosubstituted complexes derived from phenylglyoxal suggests the formation of only one pure product. The observed peaks corresponding to $M(HC{=}N{-}N{=}CSSMe)^+$, $M(PhC{=}N{-}N{=}C(S)N\langle)^+$ and $(PhC{=}N{-}N{=}C(S)N\langle)^+$ (M = Ni or Pd and N$\langle$ = Pip or Morph) fragments in their electron ionization mass spectra suggest that substitution of the –SMe group occurs on the aromatic half of the ligand and structure (**IV**, R_1 = Ph, R_2 = H) can be assigned for these monosubstituted complexes.

Although our studies on the mechanism of mono and disubstituted complexes formation are far from complete, several observations bearing on the mechanism have been made. From the present synthetic work it is quite apparent that the nickel(II) complexes (**I**) ($R_1 = R_2$ = Me, Ph and R_1 = Ph, R_2 = H) possess two types of electrophilic centers susceptible to nucleophilic attack, namely the central Ni(II) ion and the C–SMe carbons. The isolation of the monoadducts **1** and **2**, Table I, demonstrates the Lewis acidity of these complexes which is also evident from the profound spectral changes observed on the addition of pyridine to (**I**) ($R_1 = R_2$ = Me and R_1 = Ph, R_2 = H) in benzene solution.

It is expected that Lewis acid–base interactions are more kinetically favoured as compared to the substitution of the SMe group. Consequently, it can be assumed that the reaction of piperidine or morpholine with these nickel(II) complexes initially proceeds with the formation of monoadducts (**II**). Addition of the base molecule to the nickel(II) reduces its electrophilicity rendering it reluctant for bis adduct formation so that a further attack of the base occurs on the C–SMe carbon of the monoadduct so formed and results in the formation of a dipolar transition state (**VII** or **VIII**) with a tetrahedral carbon. In this transition state, the positive charge is located on the nucleophile nitrogen while the negative charge can be accommodated either on the aromatic phenyl ring of the α-diketone residue (**VII**) or on the carbon atom of the other C–SMe group (**VIII**) through extended conjugation. Elimination of MeSH molecule from (**VII**) or (**VIII**) gives rise to the monosubstituted monoadducts (**III**).

The charge density distribution in the case of an asymmetric complex (**I**) (R_1 = Ph and R_2 = H) reveals that the C–SMe carbon of the aromatic half possesses higher electrophilicity than the other C–SMe carbon, and the nucleophilic attack of piperidine or morpholine will thus occur preferentially on the aromatic half giving (**IV**) rather than (**V**) as confirmed by mass spectral studies.

Substitution of one SMe group in (**II**) by the electron releasing piperidyl and morpholyl group to form (**III**), undoubtedly reduces the formal positive charge on the Ni(II) ion, thus decreasing the axial Ni–N bond strength. Consequently, it seems reasonable to assume that the formed monosubstituted monoadducts (**III**) become thermodynamically less stable and readily lose the axially coordinated base to give the corresponding monosubstituted

complexes (**VI**). The isolation of (**3**) and (**4**) is probably due to higher Lewis acidity of Ni(Phg2-SMe) relative to Ni(Da2SMe) and Ni(Ben2SMe). It also indicates that the formation of the mono-substituted complexes (**IV**) proceeds, in general, via the monosubstituted monoadduct intermediate or transition state. Furthermore, the contribution of the dipolar structure (**VIII**) will prevent the simultaneous nucleophilic attack of the other carbon and the formation of monosubstituted complexes results in the deactivation of the remaining –CSMe group. A similar deactivation process has been reported for the reaction of $Pt(S_2COCH_2C_6H_5)_2$ with 4-methyl-piperidine [8]. It is worthwhile noting that the contribution of (**VIII**) is predominant in case of $R_1 = R_2 = Me$ and decreases in the order $R_1 = R_2 = Me > R_1 = Ph$, $R_2 = H > R_1 = R_2 = Ph$. This is in agreement with the observed decreasing tendency of M(Ben2SMe) > M(Phg2SMe) > M(Da2SMe) to form disubstituted chelates. The presence of a large excess of piperidine or morpholine affects the substitution of the second S–Me group of (**IV**) and the disubstituted complexes (**VI**) can be isolated.

Experimental

(i) Preparation of M(Da2SMe) (I, $R_1 = R_2 = Me$; M = Ni(II) or Pd(II)), M(Ben2SMe) (I, $R_1 = R_2 = Ph$, M = Ni(II) or Pd(II)) and M(Phg2SMe) (I, $R_1 = Ph$, $R_2 = H$, M = Ni(II) or Pd(II)) Complexes

These complexes were prepared as described previously [10]. The complexes prepared were crystallized from $CHCl_3$–petroleum ether (40–60 °C).

(ii) Preparation of Piperidine and Morpholine Monoadducts (1 and 2) (II, $R_1 = Ph$, $R_2 = H$, M = Ni(II))

A suspension of Ni(Phg2SMe) (0.01 mol) in dry diethylether (50 cm^3) was treated with piperidine or morpholine (0.02 mol) in diethylether (10 cm^3). The reaction mixture was stirred for 2 h at room temperature. The isolated brown insoluble monoadducts were filtered out, washed with diethylether then dried *in vacuo*.

The filtrate was concentrated to half its volume by evaporation. On cooling, the green crystals of the monosubstituted complex (**11** or **13**) (**IV**, $R_1 = Ph$, $R_2 = H$, $N\diagup$ = piperidine or morpholine and M = Ni(II)) which separated out were filtered and then dried *in vacuo*.

(iii) Preparation of the Monosubstituted Complexes (5–10, 12 and 14)

The other monosubstituted complexes were prepared by refluxing I ($R_1 = R_2 = Me$, $R_1 = R_2 = Ph$; M = Ni(II) or Pd(II) and $R_1 = Ph$, $R_2 = H$, M = Pd(II)) (0.01 mol) in dry benzene (40 cm^3) with piperidine or morpholine (0.10 mol) for 3 h. During this time, the corresponding monosubstituted complex which was separated out was filtered and crystallized from $CHCl_3$.

(iv) Preparation of the Monosubstituted Monoadducts (3 and 4)

To a solution of Ni(Phg2SMe) (0.01 mol) in dry benzene (30 cm^3), dry piperidine or morpholine (0.10 mol) was added dropwise with constant stirring. The resulting mixture was refluxed for 3 h and then evaporated to half its volume and allowed to cool for 24 h at 0 °C. The isolated product (**3** or **4**) was filtered and crystallized from $CHCl_3$.

(v) Preparation of the Disubstituted Complexes (15–21)

A solution of **I** ($R_1 = R_2 = Ph$, M = Ni(II) or Pd(II)) (0.01 mol) in benzene (50 cm^3) was treated with a 20-fold excess (0.20 mol) of piperidine. The resulting reaction mixture was refluxed for 5 h. On cooling, the disubstituted complex (**15** or **16**) which separated out was filtered and then crystallized from CH_2Cl_2. The other disubstituted chelates (**17–21**) were similarly prepared by refluxing **I** ($R_1 = R_2 = Ph$, M = Ni(II) or Pd(II)) with morpholine or piperidine (1.00 mol) in benzene (50 cm^3) for 3 h. The resulting solution was evaporated and the separated complex was filtered and then crystallized from CH_2Cl_2,

Physical Measurements

The electronic spectra of the prepared complexes, Table III, were recorded on a Pye Unicam SP 1801 spectrophotometer. The infrared spectra were made with a Schimatzu IR4 spectrophotometer. Calibration of the frequency reading was made with a polystyrene film; solid samples were examined as Nujol mulls and/or KBr discs.

^1H NMR spectra, Table II, were measured by Varian XL-100 and/or Brucker WH 400 instruments using tetramethylsilane as an internal standard.

The mass spectra were registered on a Varian MAT 711 double focusing spectrometer equipped with a direct inlet system and operating at 70 eV electron beam energy. All the spectra were recorded at the lowest possible temperature.

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