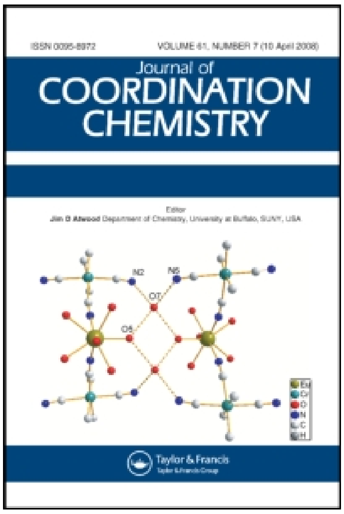

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PHENELZINE COMPOUNDS: COMPLEXES CONTAINING THE PHENELZINIUM(1+) CATION AND COMPLEXES CONTAINING THE FREE BASE

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The complexes M(phzH)$_2$(SO$_4$)$_2$ (M=Mn, Fe, Co, Ni, Zn, phzH = monoprotonated β-phenylethylhydrazine) have been isolated. Evidence from ultraviolet and infrared spectroscopy indicates that they contain six-coordinated metals bonded to phenylethylhydrazinium cations and linked to each other by double sulphato-bridges. Coordination compounds containing β-phenylethylhydrazine have been prepared of three types, MX$_2$(phz)$_2$(M=Mn, X=Br; M=Co, X=Cl, Br, I; M=Ni, X=Br, M=Zn, X=Br) MX$_2$(phz) (M=Zn, X=Cl, Br, NCS) and MX$_2$(phz)$_3$(M=Ni, X=I). Spectroscopic and magnetic methods have been used to assign structures to these compounds.

Keywords: Phenelzine, phenylethylhydrazine, complexes, synthesis coordination

INTRODUCTION

β-Phenylethylhydrazine, $C_6H_5CH_2NHNNH_2$, (phenelzine = phz), has been used as an anti-depressant drug in the form of its sulphate salt under the trade name of Nardil. Along with other hydrazine based antidepressants however, phenelzine is now known to be carcinogenic to mice.[1] Surprisingly, no compounds of phenelzine containing metal ions have been reported. The coordination chemistry of other hydrazines has attracted widespread interest.[2] We have found and report here that complexes containing the phenelzinium(1+) cation, $C_6H_5CH_2CH_2\overset{+}{N}H_2NH_2$ (phzH), can be obtained starting from phenelzine dihydrogen sulphate and metal salts in ethanol. We also report some coordination compounds of the free base phenelzine with transition metal ions.

EXPERIMENTAL

Physical measurements and analyses

Infrared spectra were measured in mulls between CsI plates using a Perkin-Elmer 577 spectrophotometer. Diffuse reflectance spectra were measured using a Perkin-Elmer 330 spectrophotometer over the range 6500–40,000 cm^{-1}. Magnetic moments were obtained by the Guoy method at room temperature. Metals were determined by EDTA titration and C,H,N analyses were carried out in this department by Mr. M. Carruthers.

Preparation of Phenelzine

(WARNING: phenelzine dihydrogen sulphate is a skin irritant; rubber gloves are essential for its handling). Phenelzine dihydrogen sulphate, $C_6H_5CH_2CH_2NHNH_2 \cdot H_2SO_4$, was prepared from 2-chloroethylbenzene and hydrazine hydrate according to the

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method of Votocek and Leminger.[3] The crude product was extracted with hot methanol in a Soxhlet apparatus and the title compound crystallised on cooling. Found: C, 40.9; H, 6.06; N, 12.0%. $C_8H_{12}N_2SO_4$ requires C, 41.0; H, 5.98; N, 12.0%.

In order to isolate the free ligand, the sulphate was dissolved in water and the solution cooled in ice during the addition of an excess of potassium hydroxide pellets. The freed base was then extracted with several portions of ether, the combined extracts being then dried with potassium hydroxide pellets prior to use in the preparation of complexes. This procedure was used in each preparation of a metal complex because stock solutions of phenelzine are susceptible to autoxidation.[4] In those preparations requiring ethanolic solutions only, the ethereal solution of phenelzine was evaporated on a rotavapor and the resulting oil diluted with ethanol.

Preparation of Phenelzinium Complexes

These were usually crystallised from ethanolic solutions of phenelzine dihydrogen sulphate and an ethanol-soluble salt of the metal. The preparation of $[Co(phzH)_2(SO_4)_2]$ is typical. Anhydrous $CoCl_2$ (2.6g) was dissolved in ethanol (50 cm^3) and a solution of phenelzine dihydrogen sulphate (0.68g) in ethanol (25 cm^3) was added. The mixture was warmed to the boiling point and then cooled to room temperature to give pink crystals which were filtered off, washed with ethanol and ether, and dried in a vacuum desiccator over silica gel. Identical crystals were obtained using $CoCl_2$ (0.17g) and phenelzine dihydrogen sulphate (0.68g). The ethanol - soluble starting materials of the other metals used were, for zinc, $ZnCl_2$, $ZnBr_2$ and $Zn(SCN)_2$; for copper, $CuCl_2$; for lithium, LiBr; for iron, $FeCl_3$, for manganese $MnBr_2$ and for lanthanum $LaCl_3 \cdot 7H_2O$. Nickel(II) and palladium(II) salts required the use of other solvents.

The nickel(II) complex was prepared by heating a solution of phenelzine dihydrogen sulphate (0.55 g, 2.3×10^{-3} mol) in a 1:1 ethanol-methanol mixture (50 cm^3) under reflux with a suspension of $NiCl_2$ (0.13g, 1×10^{-3} mol) in the same mixed solvent (50 cm^3) for 3h. After standing overnight, the mixture was filtered and the blue-green crystals washed with ether and dried in a vacuum desiccator (yield 0.49g, 94%; m p. 240°C (decomp.)).

The palladium(II) complex was prepared using phenelzine dihydrogen sulphate (0.75g, 3.2×10^{-3} mol) dissolved in ethanol (20 cm^3) to which was added $PdBr_2$ (0.21g, 0.8×10^{-3} mol) dissolved in a mixture of ethanol (20 cm^3) and conc. HCl (3.5 cm^3). The orange solution was heated under reflux for 2h and when no crystallisation occurred on cooling, the solvent was removed by evaporation and the oily residue recrystallised from a mixture of tetrahydrofuran and ether (1:4) to give yellow-brown crystals (yield 0.47g, 91%; m.p. 169°C (decomp.)).

Preparation of phenelzine complexes

Unless otherwise stated, the complexes reported in Table I were prepared by treating ethanolic solutions of the anhydrous metal salt with ethereal solutions of phenelzine. Experiments were carried out using both an excess of the anhydrous metal salt (M:L = 4:1) and an excess of phenelzine (M:L = 1:4). The amount of phenelzine used was measured by taking a known weight of phenelzine dihydrogen sulphate and assuming quantitative ether extraction after treatment with KOH. The mixtures were stirred and heated to the boiling point, after cooling the precipitated complexes were washed with ethanol and ether and dried *in vacuo*.

TABLE I
Complexes of the Phenelzinium Ion and of Phenelzine: Colours and Elemental Analyses

Compound	Colour	Elemental Analyses (%)*			
		C	H	N	M
Phenelzinium complexes					
$Mn(phzH)_2(SO_4)_2$	white	36.8(36.9)	5.04(4.99)	10.0(10.7)	
$Fe(phzH)_2(SO_4)_2$	white	34.4(36.7)	4.90(4.98)	10.9(10.7)	
$Co(phzH)_2(SO_4)_2$	pink	36.4(36.6)	4.97(4.95)	10.5(10.7)	
$Ni(phzH)_2(SO_4)_2$	blue-green	36.7(36.6)	4.96(4.96)	10.4(10.7)	
$Zn(phzH)_2(SO_4)_2$	white	36.2(36.1)	4.93(4.89)	10.4(10.5)	
$3(phzH)_2SO_4 \cdot La_2(SO_4)_3 \cdot 4H_2O$	white	33.0(33.0)	4.73(4.92)	9.60(9.61)	
$6(phzH)_2SO_4 \cdot 5PdSO_4 \cdot H_2O$	yellow-brown	35.4(35.5)	5.00(4.89)	9.69(10.3)	
$(phzH)_2SO_4 \cdot Li_2SO_4$	white	40.2(40.0)	5.59(5.41)	11.5(11.7)	
Phenelzine complexes					
$MnBr_2(phz)_2$	white	38.4(39.4)	4.88(4.93)	10.5(11.5)	11.6(11.3)
$CoCl_2(phz)_2$	pink	46.1(47.8)	5.73(4.97)	12.1(13.9)	13.8(14.7)
$CoBr_2(phz)_2$	pink	38.9(39.1)	4.83(4.89)	10.4(11.4)	12.2(12.0)
$CoI_2(phz)_2$	pink	32.9(32.8)	4.01(4.10)	8.49(9.58)	9.93(10.1)
$NiBr_2(phz)_2$	green	38.3(39.1)	4.87(4.89)	10.6(11.4)	11.7(12.0)
$NiI_2(phz)_3$	blue	41.0(40.0)	4.83(5.00)	9.63(11.6)	
$ZnCl_2(phz)$	white	35.9(35.3)	4.45(4.41)	10.1(10.3)	24.4(24.0)
$ZnBr_2(phz)$	white	27.8(26.6)	3.52(3.32)	7.99(7.75)	18.1(18.1)
$ZnBr_2(phz)_2$	white	38.6(38.6)	4.69(4.83)	10.9(11.3)	
$Zn(NCS)_2(phz)$	white	38.6(37.8)	3.87(3.78)	17.7(17.7)	20.2(20.6)

*Calculated values in parentheses.

When this method was used to prepare $MnBr_2(phz)_2$ and $NiI_2(phz)_3$, complexes with poor analytical data were obtained. This failure to produce pure complexes was attributed to the presence of traces of water in the starting materials. The pure complexes were obtained using the above method but with the addition of 2 cm^3 of triethylorthoformate as desiccant to the metal solution prior to adding the ligand. This technique has been found useful in the preparation of similar complexes with other ligands.[5]

RESULTS AND DISCUSSION

Phenelzinium Complexes

Complexes which may be formulated as double salts $(phzH)_2SO_4 \cdot MSO_4$ (M=Mn, Fe, Co, Ni and Zn) (Table I) are precipitated from ethanolic solutions of phenelzine dihydrogen sulphate and a soluble salt of the metal (not the metal sulphate which is in every case insoluble in ethanol). At first sight these salts appear to contain the sulphate of monoprotonated phenelzine rather than diprotonated phenelzine sulphate. The sulphate of monoprotonated phenelzine, *i.e.*, $(phzH)_2SO_4$, is unreported elsewhere. The spectroscopic evidence presented below however supports the contention that these compounds are not double salts containing the free phenelzinium(+1) ion but rather coordination compounds in which this cation is bonded to the metal. They are all insoluble in solvents with which they do not react. Note that the iron(II) compound was prepared from iron(III) chloride so that the phenelzinium cation acts as a reducing agent in this reaction. Our attempts to prepare a copper complex gave pale blue products with variable analytical data. It was evident that at least partial reduction to

TABLE II
Electronic Spectra and Magnetic Moments of Complexes of Phenelzinium and Phenelzine

Compound	Electronic Spectra (diffuse reflectance); $cm^{-1} \times 10^3$			μ_{eff}(BM)
	$^4T_{1g} \rightarrow {}^4T_{1g}(P)$	$^4A_{2g}$	$^4T_{2g}$	
$Co(phzH)_2(SO_4)_2$	21.4	20.0	7.6	4.90
$Co(phz)_2Cl_2$	20.1(br)		8.0	5.09
$Co(phz)_2Br_2$	19.4	17.5	8.7	5.07
$Co(phz)_2I_2$	18.3	16.9	8.3	5.15
	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$	$^3T_{1g}$	$^3T_{2g}$	
$Ni(phzH)_2(SO_4)_2$	26.0	15.4, 14.0	9.6	
$[Ni(phz)_3(SO_4)_2$	28.6	17.0	10.1	3.03
$Ni(phz)_2Br_2$	26.7	15.2	8.4	3.14
	$^5T_{2g} \rightarrow {}^5E_g$			
$Fe(phzH)_2(SO_4)$	9.8br			5.77
$Mn(phzH)_2(SO_4)_2$		(obscured)		6.10
$MnBr_2(phz)_2$		(obscured)		5.99

copper(I) was occurring. A mixed oxidation state copper complex has been reported[14] in the reaction of copper(II) chloride with hydrazinium chloride in concentrated hydrochloric acid.

The magnetic moments of the manganese(II), iron(II), cobalt(II) and nickel(II) compounds (Table II) are in agreement with their being formulated as high spin octahedral complexes. The iron(II) compound, unlike the others, is oxidised in air turning brown and the rather high moment for this compound we attribute to the presence of iron(III). The electronic spectra of the solids (Table II) are similarly assignable to a pseudo-octahedral coordination sphere around the metals and the positions of the absorption maxima are very similar to those found by Nieuwpoort and Reedijk[6] for analogous complexes of the hydrazinium cation. Little splitting of the bands is seen however with the exception of $^3T_{1g}$ band in $Ni(phzH)_2(SO_4)_2$ which is split into the ^3Eg (15,400) and $^3A_{2g}$ (14,000) components in D_{4h} symmetry. We therefore believe these compounds to have a polymeric structure with double sulphate bridges and a nitrogen atom from different phenelzinium cations occupying the apical positions above and below the plane of metal sulphato bridges. This type of structure was first discovered by Prout and Powell[7] during a two-dimensional X-ray analysis of $Zn(N_2H_5)_2(SO_4)_2$. The hydrazine ligands can thus be regarded as bridging the metal ion and a proton. A less likely structure is a monomeric unit $M(phzH)_2(SO_4)_2$ in which the sulphate groups chelate to the same metal; such a structure has been proposed for $Ni(N_2H_5)_2(C_2O_4)_2 \cdot 2H_2O$.[13]

The infrared spectra of the complexes $M(phzH)_2(SO_4)_2$ are all very similar; the important features in the spectrum of the manganese(II) complex together with those of phenelzinium(2+) sulphate and the free ligand are reported in Table III. Bands due to the C_6H_5 rings and the CH_2 chains are not listed. Unfortunately the sulphate bands are not diagnostically very helpful in assigning the mode of bonding of the sulphate ions; they are however in similar positions to those of other bridging bidentate sulphato-complexes, *e.g.*, $Cu(bipy)_2SO_4.4H_2O$[9] including those of the hydrazinium analogues of these compounds.[6] The band of most interest in complexes of hydrazine and hydrazone ligands is that due to the N-N stretch. In free hydrazine, ν(N-N) occurs[10] at 1098cm^{-1} while in complexes containing bridging hydrazine, ν(N-N) moves

TABLE III

Some Important infrared bands (cm^{-1}) in Mn(phzH)$_2$(SO$_4$)$_2$, (phzH$_2$)SO$_4$ and phz

Assignment	Mn(phzH)$_2$(SO$_4$)$_2$(mull)	(phzH$_2$)SO$_4$(mull)	phz (liquid)
ν_s(N-H)	3230	3639	3300
	3130	3418	3104
	3102	3308	3082
			3060
	3022	3022	3060
(N-H) bend	1620	1620	1601
	1601	1608	
	1579	1585	
	1568	1550	
δ(NH$_2$)	1249	1260	1260
ν(N-N)	1162	1177	1125
ν_3(SO$_4^{2-}$)	1111	1115	
	1029	1014	
ν_1(SO$_4^{2-}$)	991	964	
ν_4(SO$_4^{2-}$)	641	639	
	617	618	
	598	608	
	579	579	
(N-N) bend	461	471	496
ν_2(SO$_4^{3-}$)	434	425	
ν(M-N)	329		
ν(M-O)	240		

to the 1150 -1205 cm^{-1} region. We assign the band at 1125 cm^{-1} in phenelzine to ν(N-N); the shift of this band to higher wavenumbers observed in the phenelzinium complexes is typical of bridged hydrazine species.[10] Similarly there is a shift of ν(N-N) to higher wavenumbers in diprotonated phenelzine; this is to be expected as the lone pair donation from the nitrogen atoms to protons reduces lone pair — lone pair repulsive forces on adjacent nitrogen atoms. We are thus in agreement with Nieuwpoort and Reedijk[6] about this shift (although their actual assignment to ν(N-N) differs) but disagree with other workers[11] who in assigning the spectrum of N_2H_5Cl assert that ν(N-N) occurs at a lower frequency than in the free base. Whilst phenelzine shows no bands in the region 2858 cm^{-1} (CH$_2$) to 1600 cm^{-1} (NH) the phenelzinium(+1) complexes and phenelzinium(+2) sulphate show broad unresolved absorptions in the 2800-2400 cm^{-1} region. These are assigned to strongly hydrogen-bridged N-H stretchings; Prout and Powell[7] have shown that in $Zn(N_2H_5)_2(SO_4)_2$ the chains of sulphato bridged metal atoms are linked to other chains through hydrogen bonds between the sulphate oxygen atoms of one chain and hydrogen atoms from N_2H_5+ in another.

We conclude then that in the phenelzinium complexes nitrogen atoms from the phenelzinium(1+) cations occupy the apical positions in tetragonal coordination around the metal. However, unlike the hydrazinium(1+) coordination in $Zn(N_2H_5)_2(SO_4)_2$ there are two different nitrogen atoms in the phenelzinium cation. Further, there are two possible formulae for the cation, $C_6H_5CH_2CH_2NH\overset{+}{N}H_3$ and $C_6H_5CH_2CH_2\overset{+}{N}H_2NH_2$. Only the diprotonated base *i.e.*, $C_6H_5CH_2CH_2\overset{+}{N}H_2\overset{+}{N}H_3$ is known in salts but we believe the structure $C_6H_5CH_2CH_2N\overset{+}{H}_2NH_2$ the more likely for the monoprotonated base. Infrared studies[12] have shown that in alkyl hydrazines protonation occurs on N^1 whereas in arylhydrazines N^2 protonation occurs. Thus in phenelzinium(1+) complexes it seems likely that N^1 is protonated and N^2 bonded to the metal. Such a bonding of the phenelzinium ion is also the expected one for steric reasons.

The phenelzinium(1+) complexes of lithium, lanthanum and palladium have different stoichiometries and different infrared spectra from the complexes discussed above. We are unable to make structural conclusions about these compounds but their spectra differ principally in the $\nu_2(SO_4^{2-})$ region where higher stretching frequencies are observed than in the other phenelzinium complexes. It is possible therefore that these may be double salts of phenelzinium(1+) sulphate and metal sulphates. The lithium salt is of most interest as in medical use it combines the source of lithium for lithium therapy with the antidepressant action of phenelzine.

Phenelzine Complexes

The complexes prepared by the addition of ethereal solutions of the free base to ethanolic solutions of metal salts are listed in Table I. Only one *tris*-phenelzine complex, $NiI_2(phz)_3$, has been isolated. The magnetic and spectral data (Table II) clearly show this to be octahedral and the positions of the *d-d* bands are almost identical to those in $[Ni(N_2H_4)_3]Cl_2$ and $[Ni(CH_3NHNH_2)_6]Cl_2$[15] so that the presence of the NiN_6 chromophore is established. The most likely structure for this complex is thus that of a polymeric network of three dimensional phenelzine bridges with iodide ions outside the first coordination sphere.

Bis-phenelzine complexes (Table I) have been isolated for CoX_2 (X=Cl, Br, I) and MBr_2(M=Mn, Ni, Zn). The magnetic moments and electronic spectra clearly show the cobalt(II) and nickel(II) complexes to be pseudo-octahedral. Further, the band positions of the cobalt(II) complexes are similar to those in the methylhydrazine complexes CoX_2L_2[16] and indicate coordination by the halide ions. Similarly, the nickel(II) complex spectra are best interpreted on the basis of an NiN_4Br_2 chromophore. The *bis*-complexes thus probably have a tetragonal structure with terminal halides and bridging phenelzine. In agreement with their proposed polymeric structure these complexes are generally insoluble in solvents with which they do not react. The cobalt iodide complex $CoI_2(phz)_2$ gave a pink solution in nitromethane with absorption bands at 18,900 cm^{-1} (ε=28), 12,200 cm^{-1} (ε=5) and 8,500 cm^{-1} (ε=8); these extinction coefficients confirm the six coordinate assignment.

Mono-phenelzine complexes are formed by zinc chloride, bromide and thiocyanate; only the bromide forms a *bis*-phenelzine complex with excess ligand. This is surprising in view of the well characterised complex *bis*(hydrazine)zinc(II) chloride[17] and is presumably due to the steric effect of the phenethyl group on one of the nitrogen atoms.

The i.r. spectra of the complexes support the presence of bridging phenelzine. The spectra of the $MX_2(phz)_2$ compounds are all very similar; Table IV lists some important bands in selected compounds. The strong band in the spectra in the 1170–1200 cm^{-1} region we attribute to ν(N–N); the increase from that in the free ligand

TABLE IV
Some Important Infrared Bands (cm^{-1}) in Phenelzine Complexes

Complex	$\nu(CN)_{NCS}$	ν(NN)	δ(NCS)	νMX	$\nu MN_{(NCS)}$
$ZnCl_2(phz)$		1197		331, 289	
$ZnBr_2(phz)$		1189		265	
$ZnBr_2(phz)_2$		1192			
$Zn(NCS)_2(phz)$	2115, 2044	1188	498, 492		316
$CoCl_2(phz)_2$		1174		271, 249	

supports the bridging mode. The two Co–Cl stretches in $CoCl_2(phz)_2$ are in a lower region than that characteristically shown by tetrahedral $CoCl_2L_2$ complexes[18] and their position is consistent with the presence of terminal metal-chlorine bonds in a tetragonal structure; no Co–X stretches are observed in the bromide and iodide complexes. The *mono*-phenelzine complexes of zinc in contrast show ν(Zn–Cl) bands in a region characteristic of tetrahedral zinc complexes and ν(Zn–Br) also becomes visible. These compounds may thus contain zinc in a tetrahedral environment with terminal halogens and bridging phenelzine. The i.r. spectrum of the thiocyanate complex shows ν(M–N) and is consistent with the presence of terminal N-bonded thiocyanate groups.[19] Unlike the cobalt and nickel complex, the zinc compounds are soluble in dimethylsulphoxide and in methanol in which they behave as non-electrolytes.

The occurrence of bridging phenelzine in both six- and four-coordinate complexes is further shown in the cobalt(II) complexes. The data in Table I belie the fact that we had considerable difficulty in obtaining stoichiometric complexes of cobalt(II) halides. The pink complexes which initially were collected were found to change colour to violet and finally to blue after a few days. Unless analysed immediately after preparation, analytical data indicated stoichiometries in the range CoX_2L to CoX_2L_2. In order to investigate this change we prepared the cobalt(II) bromide complex at a higher temperature using butanol as solvent. At 118°C and in the presence of excess phenelzine, the initially pink precipitate became blue but reverted to pink upon cooling to room temperature. Whilst the spectrum of the pink compound (Table II) is clearly that of a six-coordinate cobalt(II) complex, the blue compound obtained either by heating the pink compound (in the absence of solvent or ligand) to 120°C for 30 minutes or by keeping it in a desiccator for several days, shows no band around 19,000 cm^{-1} but an intense band with shoulders appears centred at 14,500 cm^{-1} which we assign to the $^4A_2 \rightarrow {}^4T_1(P)$ transition in a pseudo-tetrahedral complex. Analytical data on the blue complexes formed in these ways were never quite stoichiometric but approached those of CoX_2L. The main changes in the i.r. spectra of the blue compound were the appearance of a peak attributable to ν(Co–Br) at 238 cm^{-1} and a shift of ν(N–N) from 1178 cm^{-1} (in the pink compound) to 1163 cm^{-1}. A larger shift in ν(N–N) would be expected if the phenelzine had become unidentate so it is concluded that it is still bridging in $CoBr_2(phz)$.

Phenelzine, like its diprotonated cation, reduces iron(III) and copper(II) halides with effervescence but we have been unable to isolate pure complexes of iron(II) or copper(I) from these mixtures.

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