

Complexes with N, S donor ligands: Part II—Nickel (II), copper (II), cobalt (II), iron (III) and palladium (II) complexes of 2, 4-bis(2'-mercaptophenylimino)-pentane and 2-(2-mercaptophenyl)imino-4-pentanone and their reactions with alkyl and aryl halides leading to the formation of macrocycles

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The *in situ* reactions of a mixture of 2, 4-pentanedione and 2-aminobenzenethiol with Ni(II) and Pd(II) salts yield complexes of the type $[M_2(MPIP)_2]$ where H_2MPIP is the schiff base 2-(2-mercaptophenyl)imino-4-pentanone obtained by condensation of one molecule of the ketone with one molecule of the amine. On the other hand, similar reactions with Co(II), Fe(III) and Cu(II) salts give the complexes $[Co(PDMPI)]$, $[Fe(PDMPI)Cl]$ and $[Cu_2(PDMPI)Cl_2]$ where H_2PDMPI is the schiff base obtained by the condensation of two molecules of the amine with one molecule of the ketone. $[Fe(PDMPI)Cl]$ smoothly reacts with bifunctional alkylating agents like 1, 2-dibromoethane and α, α' -dibromo-*o*-xylene to form the macrocyclic complexes of {S, S'-ethylene-2, 4-bis(2'-mercaptophenylimino)pentane} iron(III), $[Fe(EPDMPI)Cl]Br_2$ and {S, S'-*o*-xylyl-2, 4-bis(2'-mercaptophenylimino)pentane} iron (III), $[Fe(XPDMPI)Cl]Br_2$ respectively as a result of the alkylation of the two coordinated mercaptide groups of the complex.

In continuation of our earlier work on the metal complexes of ONS and NS donors¹⁻³, we undertook investigations on the complexes of the condensation product of 2-aminobenzenethiol with 2,4-pentanedione.

The condensation of 2, 4-pentanedione with 2-aminobenzenethiol does not produce the corresponding schiff base; instead, a benzothiazoline derivative is formed⁴. However, the benzothiazoline derivative is known to rearrange itself in the presence of metal salts to form the corresponding schiff base, 2-(2-mercaptophenyl)imino-4-pentanone, which acts as a dibasic tridentate ligand⁴⁻¹¹. The schiff base obtained by the condensation of one ketone molecule with two aminobenzenethiol molecules is expected to act as a tetradentate ligand. In the present investigation, we obtained complexes of both the types of ligands by *in situ* reactions involving the ketone, amine and the metal salts.

The *in situ* reactions of 2-aminoethanethiol, α -diketones and some metal salts have also been reported¹². It has been found that, in these reactions the metal ion acts as a template, favouring the formation of the schiff base complexes. By applying the template technique and using bifunctional

alkylating agents, synthesis of metal complexes of macrocyclic ligands has also been reported¹². Metal complexes of the condensation product of 2-aminobenzenethiol with α -diketone have also been prepared and studied¹³⁻¹⁸. In the present paper, we report the synthesis and characterisation of some metal complexes of the schiff base derived from 2-aminobenzenethiol and 2, 4-pentanedione. In order to obtain 2:1 condensation product of the amine and 2,4-pentanedione, they were allowed to react in the presence of metal salts in 2:1 molar ratio.

Materials and Methods

The analyses of C, H and N contents of the compounds were carried out using a Perkin-Elmer Model 240C elemental analyser. Analyses of metal were done by conventional methods. IR spectra were recorded in KBr discs or in solution on a Perkin-Elmer 783 spectrophotometer. The electronic spectra were recorded on a Pye Unicam SP8-150 spectrophotometer. Conductance measurements were made with a Philips PR 9500 conductivity bridge. The magnetic susceptibility measurements were carried out with a Princeton Model 155 vibrating sample magnetometer.

Molecular weight measurements were carried out with a Knauer vapour pressure osmometer.

Preparation of {2-(2-mercaptophenylimino)-4-pentanone} (H₂MPIP) and 2,4-bis(2'-mercaptophenylimino)pentane(H₂PDMPI)

The ligands could not be isolated in the pure state. Metal complexes of the ligands were prepared through the *in situ* reactions of 2-amino-benzenethiol, 2,4-pentanedione and the corresponding metal salts in 2:1:1 molar ratio.

Preparation of the metal complexes

A mixture of 2,4-pentanedione (4g, 37 mmol) and 2-aminobenzenethiol (9.36 g, 74 mmol) was stirred in an atmosphere of nitrogen for 1h and then a solution (37 mmol) of the metal chloride hydrate (acetate in case of nickel and Na₂PdCl₄ in case of palladium) in dry methanol was added to it with stirring. After the addition was completed, stirring was continued for 10-12 h.

[Ni₂(MPIP)₂] (1) and [Fe(PDMPI)Cl] (5)

Ni(CH₃COO)₂·4H₂O (6.6 g, 37 mmol) and FeCl₃ (6.6 g, 37 mmol) in dry methanol (60 cm³) was added to the mixture. The reaction mixture was filtered, and the filtrate, on evaporation produced a gummy mass. This on trituration with light petroleum ether gave the brown crystalline compound. Compound (1) was recrystallised from chloroform and compound (5) from methanol (yield, 60-65%).

[Pd₂(MPIP)₂] (2), [Co(PDMPI)] (3) and [Cu₂(PDMPI)Cl₂] (4)

Na₂PdCl₄ (19.8 g, 37 mmol), CoCl₂·6H₂O (4.45 g, 37 mmol) and CuCl₂·2H₂O (6.37 g, 37 mmol) in dry methanol (40 cm³) was added to the stirring mixture of 2,4-pentanedione and 2-aminobenzenethiol and stirred for 10-12 h. Yellow (2), deep brown (3) and deep violet (4) compounds separated out from the reaction mixtures on stirring. They were recrystallised from methanol (yield, 65-85%).

Reaction of (5) with 1,2-dibromoethane

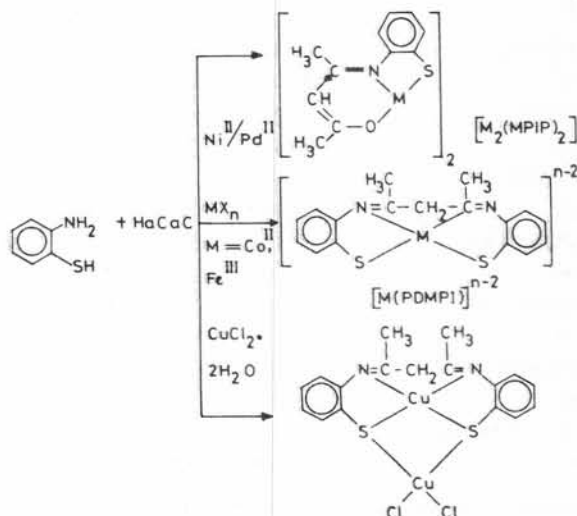
[Fe(PDMPI)Cl] (5) (1.61 g, 4 mmol) was dissolved in 1,2-dichloroethane (20 cm³) and 7.5 g (10 times excess of that required for 1:1 molar ratio) of 1,2-dibromoethane was added to the stirred solution dropwise over a period of 1/2 h. The mixture was stirred overnight and then filtered. The filtrate on concentration yielded brown microcrystals of [Fe(EPDMPI)Cl]Br₂ (6). The compound was recrystallised from methanol (yield, 60%).

Reaction of (5) with α, α'-dibromo-o-xylene

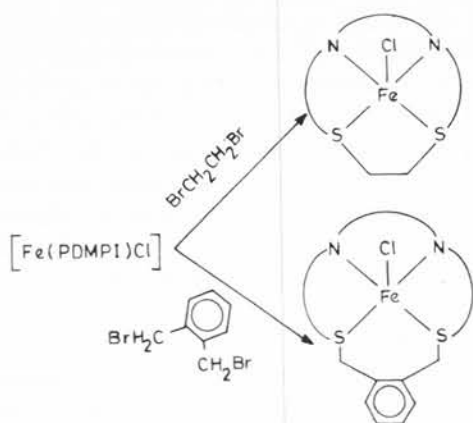
[Fe(PDMPI)Cl] (5) (1.61 g, 4 mmol) was dissolved in 1,2-dichloromethane (20 cm³) and 10 g (10 times excess of that required for 1:1 molar ratio) of α, α'-dibromo-o-xylene was added to the stirring mixture. The brown product obtained was stirred with light petroleum ether to remove excess α, α'-dibromo-o-xylene and filtered. The residue was recrystallised from methanol (yield, 60%).

Results and Discussion

All the reactions were carried out in nitrogen atmosphere and in absolute dry conditions to prevent the dimerisation of 2-aminobenzenethiol. The amine and the ketone were taken in all cases in 2:1 molar proportion with a view to condensing the two keto groups with two molecules of 2-aminobenzenethiol in presence of the metal salts to produce complexes of 2, 4-bis(2'-mercaptophenylimino)pentane, (H₂PDMPI), similar to those of biacetylbis-(mercaptophenylimine)². However, depending on the metal salts employed, both monocondensed and dicondensed products were obtained yielding thereby metal complexes of dibasic tridentate (SNO donor set) H₂MPIP and dibasic tetradentate (N₂S₂ donor set) H₂PDMPI ligands respectively (see Scheme 1). The complexes (1), (2) and (4) are sulphur bridged dinuclear species, which is supported by their molecular weight values [Found 536.6, 615.7, 518.5; calculated 527.4, 622.8 and 510.0 respectively]. Possibly due to this reason, these complexes did not react with the difunctional alkylating agents. Although the iron(III) complex (5) smoothly reacted with the alkylating agents to produce the macrocyclic complexes (see Scheme 2), the Co(II) complex (3) did



SCHEME 1



SCHEME II

not react. The failure of (3) to react with the dialkylating agents is probably due to the tetrahedral stereochemistry of the complex which may hinder such reaction.

The complexes were slightly soluble in most of the organic solvents. The analytical data of the compounds are shown in Table 1.

Electrical conductivity and magnetic moment

Most of these compounds are only slightly soluble in common organic solvents, but are freely soluble in DMF. Molar conductance values of the complexes, except (6) and (7), indicate that they are non-electrolytes which support their formulations. Complexes (6) and (7) are 1:2 electrolytes. Magnetic moment of 1.05 BM at room temperature for the

copper (II) complex (4) suggests its binuclear structure with Cu-Cu interaction. The iron(III) complexes have moments (3.98 BM) which suggest $S=3/2$ as the ground state. The quartet state apparently indicates the five-coordinate square-pyramidal stereochemistry of the complexes¹⁹⁻²¹. The magnetic moment of 4.92 BM for [Co(PDMPI)] (3) suggests tetrahedral geometry for the complex. The conductivity and magnetic moment data are compiled in Table 1.

Infrared spectra

All the complexes show the C=N stretching frequencies in the region 1595-1640 cm^{-1} . The complexation of H_2MPIP in the enol form can be inferred from the observation of two bands at 1680 and 1640 cm^{-1} in the complexes (1) and (2) which are assigned to discrete C=C and C=N stretching frequencies respectively²². Bands in the region 440-560 cm^{-1} can be assigned to M-N stretching modes based on assignments made on metal amine complexes²²⁻²⁸. Similarly, bands in the region 310-400 cm^{-1} are tentatively assigned²⁹⁻³² to $\nu_{\text{M-S}}$ in all the complexes excepting compound (1). Presence of S-bridging in these complexes may be responsible for shifting of this absorption. Other bands for [Cu₂(PDMPI)Cl₂] (4) and the iron(III) complexes in the region 340-380 cm^{-1} are due to M-Cl stretching modes²². Appearance of these bands in the metal complexes supports their proposed structure.

Table 1—Characterization data of the complexes

Compound	Found (Calc.), %						Λ_M ($\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$)	μ_{eff} (BM)
	C	H	N	Metal	Cl	Br		
[Ni ₂ (MPIP) ₂] (1)	50.82 (51.02)	4.29 (4.25)	5.43 (5.41)	22.73 (22.69)	—	—	4.43 ^a	Diamagnetic
[Pd ₂ (MPIP) ₂] (2)	42.40 (42.42)	3.51 (3.53)	4.54 (4.50)	34.20 (34.17)	—	—	16.46 ^b	Diamagnetic
[Co(PDMPI)] (3)	55.30 (55.30)	4.32 (4.34)	7.60 (7.59)	15.88 (15.97)	—	—	25.5 ^b	4.92
[Cu ₂ (PDMPI)Cl ₂] (4)	40.12 (40.16)	3.17 (3.15)	5.50 (5.51)	24.89 (25.00)	13.93 (13.98)	—	35.06 ^b	1.05
[Fe(PDMPI)Cl] (5)	50.78 (50.81)	3.96 (3.98)	6.97 (6.97)	13.88 (13.95)	8.78 (8.84)	—	39.76 ^b	4.04
[Fe(EPDMPI)Cl]Br ₂ (6)	38.70 (38.68)	3.42 (3.39)	4.91 (4.75)	9.68 (9.50)	5.98 (6.02)	26.80 (27.14)	149.72 ^b	3.98
[Fe(XPDMPI)Cl]Br ₂ (7)	44.43 (44.48)	3.53 (3.56)	4.18 (4.15)	8.40 (8.30)	5.30 (5.26)	23.82 (23.72)	153.36 ^b	4.14

^a Measured in nitromethane; ^b Measured in DMF.

For the iron(III) macrocyclic complexes [Fe(EPDMPI)Cl]Br₂ (6) and [Fe(XPDMPI)Cl]Br₂ (7), new bands in the region 610-675 cm⁻¹, which do not appear for [Fe(PDMPI)Cl] (5), are assigned to νS-CH₂ modes, supporting thereby the formation of the macrocyclic derivatives.

Electronic spectra

In the visible region, the nickel complex (1) has a small shoulder at 27027 cm⁻¹ which is assigned to ¹B_{1g} ← ¹A_{1g} transition. The strong sharp band at about 20000 cm⁻¹ is possibly due to the coupling of the ¹A_{2g} ← ¹A_{1g} band with the charge transfer band in the same region. A band at 21029 cm⁻¹ for the palladium (II) complex (2) is assigned to ¹A_{2g} ← ¹A_{1g} (d_{x²-y²} ← d_{xy}) transition in square planar geometry.

In tetrahedral environment for cobalt(II) complexes the ν₂[⁴T₁(F) ← ⁴A₂] and ν₃[⁴T₁(P) ← ⁴A₂] transitions appear as multiple absorptions in the near infrared and visible regions respectively³³. In the complex (3), ν₃ is observed at 17857 cm⁻¹ as a shoulder. The near IR band is not observed in the range of the instrument used.

In [Cu₂(PDMPI)Cl₂] (4), a band is observed at 19601 cm⁻¹ which is characteristic of a square planar copper(II) complex³³⁻³⁵. Appearance of a strong absorption band at 20202 cm⁻¹ in the spectrum of [Fe(PDMPI)Cl] (5) suggests penta-coordinated Fe(III) in the complex, as no such bands are generally observed for 6-coordinate Fe(III) complexes due to spin-forbidden transitions³⁶. Other transitions in the higher region are of charge transfer origin. For the macrocyclic complexes (6) and (7) also, the same arguments can be put forward since strong absorptions are observed at 20109 and 20080 cm⁻¹ respectively.

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