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N. Thiocarbamoyi N'. Phenylguanyl Hydrazine and its Metal Complexes*

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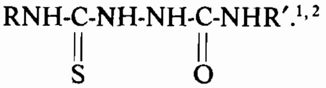
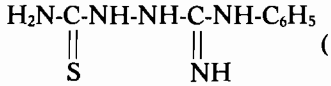
A study of N.thiocarbamoyl N'.phenylguanyl hydrazine as complexing ligand and its Ni, Cu(II), Zn, Cd, Pd(II) and Bi complexes is described. The ligand is dibasic in complexes of Cu, Pd and Bi. In other cases the ligand is monobasic but does not form 1:2 complexes. In the latter case, bonding of nickel complex is different from the rest. Ultraviolet, visible and i.r. spectra of the ligand and the metal complexes, and magnetic and conductance properties of the latter are discussed.

Introduction

Authors have studied a series of ligands of the general formula  $RNH\text{-}\underset{\underset{S}{\|}}{C}\text{-}NH\text{-}NH\text{-}\underset{\underset{O}{\|}}{C}\text{-}NHR'$.[1,2] Earlier, ligand with another thiocarbamoyl group in place of the carbamoyl group has been studied.[3-5] Authors now describe a ligand in which a phenylguanyl group replaces the carbamoyl group,



$$H_2N\text{-}\underset{\underset{S}{\|}}{C}\text{-}NH\text{-}NH\text{-}\underset{\underset{NH}{\|}}{C}\text{-}NH\text{-}C_6H_5 \quad \text{(TPGH or L)}$$

This investigation brings out a useful comparison of the three similar series of ligands, it is hoped.

The present communication describes nickel, copper(II), zinc, cadmium, palladium(II) and bismuth complexes of the ligand and some of their physical properties.

Experimental Section

Preparation of N.thiocarbamoyl N'.phenylguanyl hydrazine. The ligand was prepared from phenylcyanamide and thiosemicarbazide in hydrochloric acid, following the method of Arndt and Tschenscher.[6] M.P. 146-148°C. Phenylcyanamide was prepared in this laboratory according to the method of Hoffmann.[7]

Preparation of the complexes. An aqueous solution of the metal salt (0.005 mole) was added dropwise to a warm aqueous solution of the ligand (0.020 mole). The separated solid was digested on water bath for about half an hour, filtered, washed with water, dried in vacuum and analysed. Palladium and bismuth complexes could be recrystallized from chloroform.

Physical measurements and other experimental details. These were same as described in our previous communications.[1,2]

Results and Discussion

It is apparent from Table I that the ligand is dibasic with metals of high ionisation potential (copper(II), palladium(II) and bismuth) and monobasic in other cases (nickel, zinc and cadmium). Accordingly, complexes of three different compositions have been isolated—ML, $(M(LH))_2SO_4.xH_2O$ and M_2L_3 where LH_2 = ligand.

The ligand essentially consits of a thiourea and a guanidine unit. By analogy with guanidines, the guanidine unit of the ligand may be assumed to be protonated in acidic and aqueous(+) solutions. The band at 270 mμ of deprotonated phenylguanidine[8] naturally undergoes hypsochromic shift on protonation. With this ligand the band merges with π→π* band due to thiourea unit. The guanidine unit of TPGH is deprotonated in ethanol and in aqueous solution at higher pH. The π→π* bands of TPGH in ethanol (Table II) corresponds to those of thiourea and phenylguanidine.[8,9] In alkaline solution, the C=S group is assumed to be enolised (at least partly as the buffering action of the ligand may prevent complete enolisation and ionisation) and then both the π→π* bands seem to undergo red shift; position of the two apparant bands cannot be located with confidence from the somewhat flat broad band beyond 230 mμ on the longer wavelength side. From the positions of bands in acidic and aqueous solution it seems that there is no interaction between the two units over the central N-N bond.

(*) Abstracted from P.K.M.'s doctoral thesis, University of Calcutta.
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(+) pH of aqueous solution of the ligand is 8.93 and pK_a is found to be 6.60.
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Table I. Analysis Data of N-thiocarbamoyl N′-phenylguanyl hydrazine and its metal complexes with their colour and m.p./d.p.

Formula	Colour	Metal	Nitrogen	Sulphur	m.p./d.p. °C	μ_{eff}
$[Ni(C_8H_{10}N_5S)]_2SO_4.4H_2O$	Grey	16.57 (16.73)	20.12 (19.97)	13.52 (13.69)	[a]	Diamagnetic
$Cu(C_8H_9N_5S)$	Black	23.72 (23.50)	26.07 (25.87)	12.18, 11.97 (11.83)	135°	1.53[b]
$[Zn(C_8H_{10}N_5S)]_2SO_4.6H_2O$	White	17.35 (17.41)	18.50 (18.69)	13.12 (12.78)	185°	—
$[Cd(C_8H_{10}N_5S)]_2SO_4.4H_2O$	White	28.10 (27.80)	17.05 (17.31)	12.05 (11.87)	250° (d) yellow	—
$Pd(C_8H_9N_5S)$	Orange		22.15 (22.31)	10.84 (10.20)	165° (d)	Diamagnetic
$Bi_2(C_8H_9N_5S)_3$	Violet		19.84 (20.21)	C-27.31 (27.72) H-2.62 (2.60)	152°	—
$C_8H_{11}N_5S(L)$	White		33.27, 33.38 (33.49)	15.01 (15.31)	146-148°	—

Figures in the parentheses are the required percentages. [a] Could not be determined. [b] Diamagnetic correction per ligand molecule. $100{\cdot}8 \times 10^{-6}$ c.g.s unit.

Table II. Spectral Data of N-thiocarbamoyl N′-phenylguanyl hydrazine and its metal complexes

Compound	Solvent	λ_{max} (mμ)	Frequency (cm^{-1})	ε_{max}
Ligand	Ethanol	220	45455	11961
		~245	40816	11858
		272	36765	13604
Ligand	0.1M HCl- aqueous	206	48544	22280
		242	41322	20000
		~315	31746	676
Ligand	Water	203	49261	23000
		242	41322	18400
		~285	35088	851
Ligand	0.1M NaOH- aqueous	218	45872	16100
		~255	39216	12300
		~275	36364	10220
		~300	33333	6000
$[Ni(C_8H_{10}N_5S)]_2SO_4.4H_2O$	Ethanol	244	40984	18650
		~360	27778	251
		~430	23256	275
		660	15152	111
	Pyridine	~430	23256	11800
		655	15267	3000
$Cu(C_8H_9N_5S)$	Ethanol	218	45872	18450
		~270	37037	12630
		290	34483	15880
		~320	31250	8000
		~390	25641	1349
		534	18727	345
	Pyridine	~690	14493	50
$[Zn(C_8H_{10}N_5S)]_2SO_4.6H_2O$	Ethanol	216	46296	19210
		287	34843	25800
$Pd(C_8H_9N_5S)$	Ethanol	227	44053	21610
		275	36364	18700
		~320	31250	5840
		~380	26316	607
		500	20000	213
	Nitro-Benzene	425	23529	440
		500	20000	257
	Pyridine	510	19608	188
$[Cd(C_8H_{10}N_5S)]_2SO_4.4H_2O$	Ethanol	226	44248	14344
		265	37736	14956
		290	34483	16451
$Bi_2(C_8H_9N_5S)_3$	Cloroform	~205	48780	4350
		215	46512	5441
		270	37037	29580
	Dimethylformamide	400	25000	354

Some delocalisation appears in alkaline solution. On the basis of the positions of $\pi \rightarrow \pi^*$ bands the complexes can be divided into two groups from their uv-spectra—copper, zinc, cadmium, palladium and bismuth belong to the first and nickel to the second. In the first group there is only one $\pi \rightarrow \pi^*$ band at 270 ~ 290 mμ; band of copper complex has suffered maximum red shift and those of palladium and bismuth least. The reason for

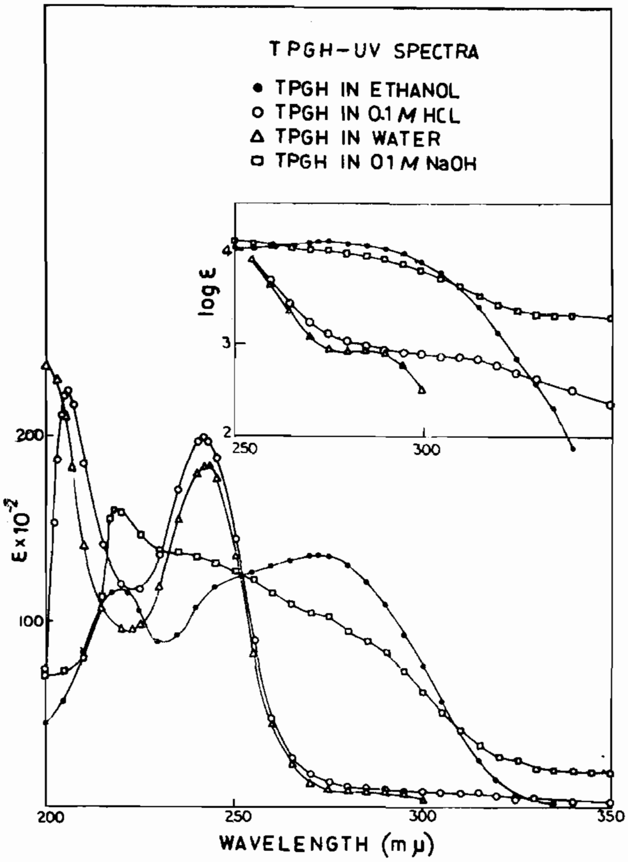

Figure 1. uv spectra of N-thiocarbamoyl N′-phenylguanyl hydrazine

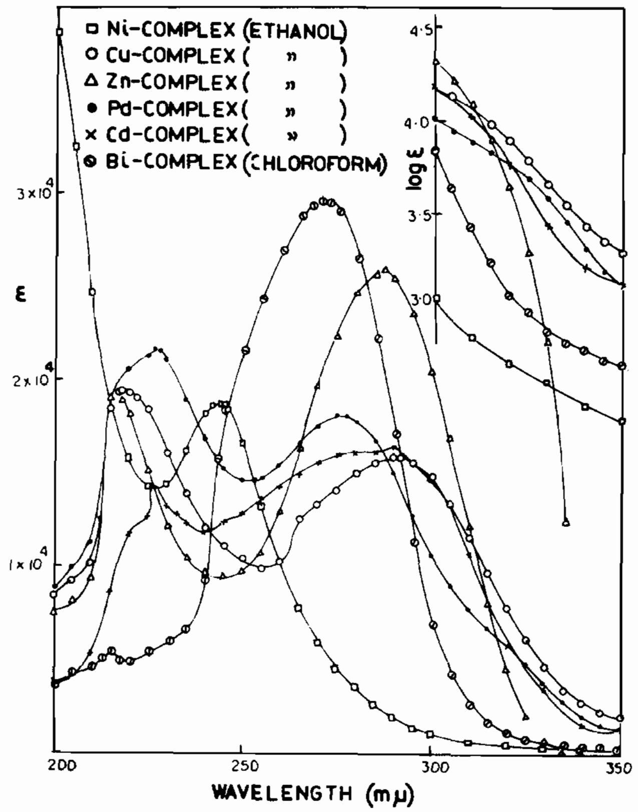

Figure 2. uv spectra of metal complexes of N-thiocarbamoyl N′-phenylguanyl hydrazine

Table III. Summary of Infra-red Bands of N-thiocarbamoyl N′-phenylguanyl hydrazine and its metal complexes

Ligand	Ni-complex	Zn-complex	Cu-complex	Pd-complex
3515 m	3480 mb	3480 mb	3475 mb	3475 mb
3400 m				
3330 m	3340 mb	3355 mb	3350 mb	3340 mb
3215 sh				
3175 m	3190 mb	3150 wb		3170 wb
1660 m		1642 sh		
1640 w		1635 s		1635 sh
1625 sh	1625 m		1620 sh	1620 m
1610 s				
1590 s	1590 s	1592 m	1590 s	1590 m
1570 s				
1560 sh	1535-1560 b	1562 sh	1545-1560 mb	1555 s
1540 kink		1547 m	1530 sh	
1490 sh	1490 s	1495 m	1480-1490 mb	1490 m
1380 w	1402 s	1402 m	1400 m	1400 m
1275 w	1285 m	1270 sh	1285 m	
	1260 m	1242 m	1240 m	1250 m
1218 m	1210 m	1212 w	1210 w	1205 w
	1130 w	1132 sh(?)		1130 vw
1105 w				
1045-1065 wb	1085 w	1085 w	1085 w	1080 vw
1020 w(?)	1050 w	1050 w		1050 vw
	980 sh(?)			
950 w	960 w			
	917 w	900 vw	905 vw	
	880 w	875 vw		840 vw
805 w	820 wb			750 sh
752 m	740 m	750-715 wb	750-720 b	740-725 b
		(725 head)		
710 m	710 m			
698 m	683 m	690 w	689 w	685 wb
685 m	655 sh			

the latter could be a restoration of energy equilibrium through a metal-ligand charge transfer. On the other hand, nickel complex of the second group shows the only $\pi \rightarrow \pi^*$ band at 245 mμ, almost the expected position of non-enolised thiourea unit. The highest energy ligand transition apparently undergoes hypsochromic shift in the second group and bathochromic in the first. Destabilisation of non-bonding electrons caused by enolisation of $C=S$ can lower the said transition. For the same reason the $n \rightarrow \pi^*$ transition can also be lowered which again is observed in the first group. It seems, therefore, that copper, zinc, cadmium, palladium, and bismuth are linked with sulphur in the enolised form and nickel, if linked at all, with non-enolised form of the group concerned in the respective complexes.

The above conclusion can also be reached from infrared spectra of a representative number of complexes (Table III). Infrared bands definitely suggest that some difference of bonding exists between copper and palladium as well as zinc, and nickel complexes. Corresponding to ligand band at 1660 cm^{-1} assigned to ν(CN),[10] zinc complex shows a band as high as 1645 cm^{-1} and others at 1625 cm^{-1}. This may be due to participation of guanyl$=$NH as a coordinate site only in zinc complex. Otherwise, spectra of zinc complex is similar to those of copper and palladium. Broad and diffused bands in the region of 3 μ suggests hydrogen-bonding which is more prominent in complexes than in ligand. The 730 cm^{-1} band of thiourea (ν(NCS) with ν(CS) as the principal contributor[11]) shifts to 755 cm^{-1} in TPGH. The usual splitting and shift to lower wavenumber[11] is observed with all but nickel complex. Similarly the band at 1416 cm.$^{-1}$ of thiourea may have shifted to higher wavenumber to merge with nujol band. The band at 1490 cm^{-1} in complexes assigned to ν_a(NCN) (guanidine unit) is a single sharp peak in zinc complex whereas in other complexes the band is either broad or split. There is no $C=NH$ group outside the chelate ring, but in a conjugated cyclic form, it seems.[12] Bands in the region of 800-1200 cm^{-1} are of weak nature and they have poorer value in identification. There is no firm evidence of sulphur coordination in nickel complex. It is difficult to identify bands responsible for free or coordinated sulphate because of other vibrations in the accepted region.[13] Nickel, zinc and cadmium complexes are non-conductors which suggest bicoordinated sulphate and we presume the same. Tests for sulphate are positive after boiling the complex with hydrochloric acid.

Nickel and palladium complexes are diamagnetic. Low magnetic moment of copper complex suggests anti-ferromagnetic properties and possibly a polymeric structure. Low solubilities of nickel, copper and zinc complexes also suggest the polymeric nature.

Early part of the visible spectra of the complexes are apparently the tail of a stronger band ($\pi \rightarrow \pi^*$ or charge transfer band?). Some of the uv-bands show higher oscillator strengths in complexes than in ligand and some are unsymmetrical. Charge transfer bands may be merged with ligand bands. π-interaction in complexes appears from their uv-spectra. In the visible region. only $d \rightarrow d$ transitions are observed. Planar configurations of the complexes are easily perceptible (Table II). Spectra of nickel and palladium complexes are independent of solvent and that of copper is dependent. π-interaction is quite strong in former case (not through sulphur in nickel complex). The visible spectra of these complexes are similar to those of N.thiocarbamoyl N'.carbamoyl hydrazine and its derivatives described earlier.[2] From the positions of the composite bands it appears that both the types of ligands offer similar ligand strength, although without the solid state spectra and gaussian analysis of the bands proper evaluation of ligand strength and bonding scheme is not possible. Replacement of oxygen by $=$NH group has not altered the ligand strength very much, it seems; a significant change in σ-bonding may not be expected but a definite increase in π-bonding capacity is expected increasing the 'soft'ness[14] of TPGH. When TPGH is monobasic, $=$NH serves as the valency link for the 'soft/hard acid' Ni^{++} while sulphur serves the same purpose for the 'soft acid' Cd^{++} and the 'soft/hard acid' Zn^{++}, there being no ligand field stabilisation in the latter case. On the other hand, the 'soft acid' copper(I), in 1:2 cationic complexes of N.thiocarbamoyl N'.carbamoyl hydrazine and its derivatives,[1,2] shows a definite (and usual) preference for sulphur—not oxygen—coordination;(‡) spectra of only palladium complexes of these ligands[1,2] are independent of solvent. However, TPGH is either monobasic or dibasic and others are always dibasic. Sulphur and guanyl nitrogen in the former case, and sulphur and oxygen in the latter case serve as the valency link. Complexes of both the types of ligands tend to be polymeric and are planar.

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(‡) The structure of the cationic complex depicted in Ref. (1) is slightly in error; one of the link should be through sulphur and the other one through the favourably placed nitrogen.