

## Synthesis and structural studies on Ni(II) chloride complexes of N,N'-(substituted) formamidino-N''-(substituted) carbamides and thiocarbamides

K L MADHOK

Centre for Rural Development and Appropriate Technology, Indian Institute of Technology, Delhi Hauz Khas, New Delhi 110 016, India

MS received 16 October 1981 ; revised 10 December 1981

**Abstract.** Nickel(II) chloride reacts with N,N'-diarylformamidino-N''-arylcabamides, thiocarbamides and N-benzoylformamidino-N''-arylcabamides, thiocarbamides forming complexes of the general formula  $[\text{Ni}(\text{Ar}, \text{NH.C}(\text{NH})\text{NH.C.X.NH.R})_2] \text{Cl}_2$  (R = phenyl, orthotolyl and paratolyl ; Ar = benzoyl ; X = S, O) and  $[\text{Ni}(\text{R.NH.C.X.NH.C}(\text{N.Ph.})\text{NH.Ph.})_2] \text{Cl}_2$  (R = phenyl, orthotolyl, paratolyl ; Ph = phenyl ; X = S, O). The ligands when oxidized with iodine undergo ring closure to related 3,5-diaryl-amino 1,2,4-thiadiazolidines and 3,5-diaryl-amino-1,2,4-diazolidines, while the complexes are not susceptible to oxidation. This confirms the binding in complexes is through sulphur and oxygen of the ligands.

**Keywords.** Nickel(II) chloride complexes ; potentiometric oxidations ; 3,5-diaryl-amino-1,2,4-thiadiazolidines ; 3,5-diaryl-amino-1,2,4-diazolidines.

### 1. Introduction

Metal complexes of sulphur donor ligands have received great attention during recent years (Horsfall and Rich 1951) because of their versatile use as antifungal and antibacterial agents. A survey of literature reveals that compounds containing both C=O and C=S groups possess significant fungicidal activity (Horsfall and Rich 1951). Despite the fact that a variety of sulphur donor ligands have been studied (Akbar Ali and Livingstone 1974 ; Mishra 1980 ; Srivastava and Madhok 1978 ; Madhok and Srivastava 1980), for the synthesis of metal complexes it appears that N,N'-(substituted) formamidino-N''-(substituted) carbamides (DSFSC) and N,N'-(substituted) formamidino-N''-(substituted) thiocarbamides (DSFSTC) having both C=O and C=S with =NH groups, has not been used. In continuation of our earlier work (Srivastava and Madhok 1978 ; Madhok and Srivastava 1980) on metal chelates of substituted thioureas, thiobiurets, the present paper describes the studies of Ni(II) chloride complexes of the title ligands.

### 2. Experimental

All the chemicals used were either BDH 'AnalaR' quality or E Merck GR reagent. Alcohol and dimethylformamide were distilled before they were used.

The ligands N,N'-diphenylformamidino N'-phenylcarbamide (DPFPC), N,N'-diphenylformamidino N'-phenylthiocarbamide (DPFPTC), N,N'-diphenylformamidino N'-orthotolylthiocarbamide (DPF.o.TTC), N,N'-diphenylformamidino N'-paratolylthiocarbamide (DPF.p.TTC), N-benzoylformamidino N'-phenylcarbamide (BFPC), N-benzoylformamidino N'-phenylthiocarbamide (BFPTC), N-benzoylformamidino N'-orthotolylthiocarbamide (BF.o.TTC) and N-benzoylformamidino N'-paratolylthiocarbamide (BF.p.TTC) were prepared by the method as described earlier (Srivastava and Madhok 1978). The purity of ligands was checked by sharp melting point and elemental analysis.

### 2.1. General method of the preparation of complexes

Standard alcoholic solution (0.1 M) of nickel chloride (200 ml) was mixed together with 200 ml of (0.2 M) alcoholic solution of the ligands and refluxed at 70° C for about 2 hr. It was then allowed to cool during which a silver grey precipitate was obtained which was analysed after being dried *in vacuo*. Melting points of these complexes were determined in open capillary tubes on a unimelt temperature apparatus and are uncorrected. In all the complexes, nickel was estimated as dimethylglyoximate nickel(II). Sulphur and chlorine were estimated by standard methods (Clarke 1960; Erdy 1965). The analytical results are recorded in table 1.

Table 1. Analytical results of Ni(II) chloride complexes.

Compound	% Ni found (calc.)	% Cl found (calc.)	% S found (calc.)	Molar conductance	
				Molarity (M)	Conductance cm <sup>2</sup> mol <sup>-1</sup> Ω <sup>-1</sup>
[Ni (DPFPTC) <sub>2</sub> ] Cl <sub>2</sub>	7.153 (7.134)	8.662 (8.642)	7.692 (7.789)	0.10 × 10 <sup>-3</sup>	150
[Ni (DPFPC) <sub>2</sub> ] Cl <sub>2</sub>	7.399 (7.432)	8.980 (8.991)	.. ..	0.10 × 10 <sup>-3</sup>	148
[Ni (DPF.o.TTC) <sub>2</sub> ] Cl <sub>2</sub>	6.955 (6.907)	8.420 (8.356)	7.555 (7.532)	0.12 × 10 <sup>-3</sup>	152
[Ni (DPF.p.TTC) <sub>2</sub> ] Cl <sub>2</sub>	6.955 (6.907)	8.486 (8.356)	7.700 (7.532)	0.11 × 10 <sup>-3</sup>	158
[Ni (BFPTC) <sub>2</sub> ] Cl <sub>2</sub>	8.100 (8.089)	9.820 (9.786)	11.155 (11.100)	0.12 × 10 <sup>-3</sup>	160
[Ni (BFPC) <sub>2</sub> ] Cl <sub>2</sub>	8.488 (6.463)	10.300 (10.230)	.. ..	0.10 × 10 <sup>-3</sup>	157
[Ni (BF.o.TTC) <sub>2</sub> ] Cl <sub>2</sub>	7.890 (7.787)	9.550 (9.421)	8.932 (8.892)	0.11 × 10 <sup>-3</sup>	149
[Ni (BF.p.TTC) <sub>2</sub> ] Cl <sub>2</sub>	7.800 (7.787)	9.389 (9.421)	8.888 (8.892)	0.12 × 10 <sup>-3</sup>	150

The magnetic susceptibility of the chelates was determined by Gouy's magnetic balance applying a field strength of about  $4.5 \times 10^3$  gauss. Mercury(II) tetra-thiocyanatecobaltate(II)  $[\text{Hg Co}(\text{CNS})_4]$  was used as the standard.

The infrared spectra of the ligands and complexes were recorded in KBr pellets on Perkin Elmer grating infrared spectrophotometer model 237-B in the range of  $4000\text{--}650\text{ cm}^{-1}$  using the pellet technique. The spectra are complicated and difficult to interpret, however only those peaks that could be assigned with reasonable certainty are listed in table 3.

The solubility of all these complexes is high in dimethylformamide. Thus the conductance measurements were carried out in freshly distilled dimethylformamide solution, on conductivity meter type LBR of Wissenschaftlich Technische, Werkstätten, Germany, with dip type cell. The solutions of the complexes were prepared immediately before use.

Studies on oxidation of ligands and their complexes were carried out with iodine solution in tetrahydrofuran using calomel and platinum electrodes. 20 ml of  $M/500$  solution in THF of the ligands and their metal complexes were titrated with  $M/50$  iodine solution in THF.

Absorption spectra of Ni(II) chloride complexes were measured by the standard method using Perkin-Elmer UV-VIS spectrophotometer model 139. Ethanol and methanol used were of BDH AnalaR quality and distilled before use. The absorption bands of Ni complexes in ethanol and methanol are represented in table 2. Transition energy  $E_T$  was calculated from the relation

$$E_T = \frac{2.859 \times 10^5}{\lambda_{\text{max}} \text{ (in } \text{Å})},$$

and the oscillatory strength  $f$  was calculated from the following equation:

$$f = 4.32 \times 10^{-19} \int E d\nu,$$

utilizing

$$E_{\text{max}} \Delta\bar{\nu} = \int E d\nu$$

where  $\Delta\bar{\nu}$  is the wave number of the half band width. All the data are recorded in table 2.

### 3. Results and discussion

All the complexes are coloured. Complexes are insoluble in most of the common organic solvents but are soluble in excess of alcohol, tetrahydrofuran and dimethylformamide. All the complexes decomposed on heating above  $160^\circ\text{C}$ , complexes are also decomposed by mineral acids.

Magnetic susceptibility of the complexes is found in the range of  $-0.285$  to  $-0.500 \times 10^{-6}$  g. The negative susceptibility values are indicative of the diamagnetic nature of the complexes.

The observed values of molar conductance in DMF are in the range of 148–160 mhos. The molar conductance results indicate the electrolytic nature of the complexes and corresponds to 1 : 2 electrolytic nature (Nicholson and Sutton 1969).

Table 2. UV spectral data on ligands and their Ni(II) chloride complexes in ethanol and methanol.

Compound	Ethanol				Methanol			
	Molarity ( $\times 10^{-5}$ )	$\lambda_{\max}$	$E_{\max}$ (k. cal. mole $^{-1}$ )	$f$	Molarity ( $\times 10^{-5}$ )	$\lambda_{\max}$	$E_{\max}$ (k. cal. mole $^{-1}$ )	$f$
BFPTC	9.485	265	85170	.1375	..	263	81550	.1109
NiCl $_2$ .2BFPTC	..	320	13290	.2935	9.990	318	12800	.2886
BFPC	..	265	87540	.0504	..	250	84010	.0555
NiCl $_2$ .2BFPC	6.172	308	12300	.1990	3.290	307	11940	.1069
BF.o.TTC	..	261	91520	.0810	..	248	83660	.0619
NiCl $_2$ .2BF.o.TTC	9.780	305	12780	.3639	3.586	305	11570	.1016
BF.p.TTC	..	263	84450	.1039	..	257	72830	.0418
NiCl $_2$ .2BF.p.TTC	8.222	320	14180	.3378	3.364	320	13820	.1336
DPFPTC	..	246	25020	.8518	..	245	19890	.0483
NiCl $_2$ .2DPFPTC	4.923	344	26090	.6415	3.610	342	22590	.4524
DPFTC	..	247	30100	1.1820	..	248	26430	.5418
NiCl $_2$ .2DPFPC	5.335	347	28770	.7450	2.290	345	25780	.3670
DPF.o.TTC	..	263	31000	.1250	..	240	27800	.6230
NiCl $_2$ .2DPF.o.TTC	6.545	308	29780	.2000	2.150	342	26400	.5290
DPF.p.TTC	..	246	31200	.1320	..	257	29300	.5582
NiCl $_2$ .2DPF.p.TTC	7.888	347	29800	.7590	2.000	325	28150	.1496

Table 3. IR spectral data of ligands and their Ni(II) chloride chelates (in  $\text{cm}^{-1}$ ).

Compound	=NH stretch	C=O stretch	N-H bend	C-H stretch	C-N stretch +N-H bend + (C=S) bend	(C=S) stretch	C=S stretch
DPFFTC	3385s	..	1641vw	1540s	1441vw	1225m	729m
NiCl <sub>2</sub> .2DPFFTC	3280mb	..	1635s	1585s	1485s	1225m	718m
DPFFC	3400s	1735w	1440m	1582m	1660m	1260m	..
NiCl <sub>2</sub> .2DPFFC	..	1720w	1630m	1470w	1422m	1222m	..
DPF.o.TTC	3402s	..	1660m	1540m	1430s	1270m	760b
NiCl <sub>2</sub> .2DPF.o.TTC	..	..	1648s	1552m	1405s	1258m	745m
DPF.p.TTC	3400s	..	1600s	1566m	1441m	1220m	756m
NiCl <sub>2</sub> .2DPF.p.TTC	..	..	1625w	1575m	1460w	1205b	740m
BFPTC	3400s	1700m	1680s	1550s	1413s	1227s	716w
NiCl <sub>2</sub> .2BFPTC	3310b	1700m	1630s	1595m	1480w	1215m	702m
BFPC	3360s	1725m	1685s	1550m	1440s	1280w	..
NiCl <sub>2</sub> .2BFPC	..	1710m	1635vw	1590m	1440ms	1255ms	..
BF.o.TTC	3400ms	1698m	1625sb	1525w	1400m	1775w	750m
NiCl <sub>2</sub> .2BF.o.TTC	3300m	1698m	1605m	1520w	1475w	1150ws	730w
BF.p.TTC	3400s	1700m	1625s	1563s	1440m	1282s	799w
NiCl <sub>2</sub> .2BF.p.TTC	3270m	1700m	1620m	1570m	1445wb	1266m	778w

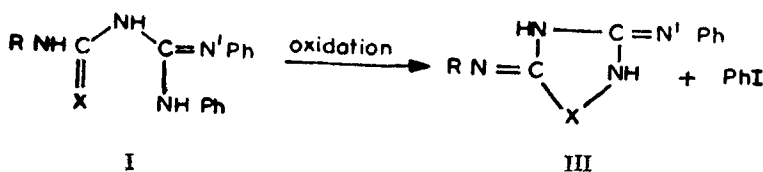
s = strong, m = medium, b = broad, w = weak.

On an examination of UV spectra of the ligands and complexes in alcohol, it is observed that the absorption band of the ligands (DPFFTC), (DPF.o.TTC, DPF.p.TTC, BFPTC, BF.o.TTC and BF.p.TTC), 240-265 nm in ethanol and methanol has been shifted to 305 to 347 nm in complexes. This shift is attributed to the fact that during the complex formation  $\pi^*$  energy level is longer due to stabilization of the excited state, so the  $n-\pi^*$  transition is shifted to lower wavelength, i.e., lower frequency and consequently lower energy. This also accounts for the fact that thiocarbonyl group is acting as donor in the complex formation. In case of DPFFC and BFPC complexes the  $\pi-\pi^*$  transitions (247-265 nm) band is shifted to lower wavelength 307 to 347 nm.

From the infrared spectra of the ligands and their metal chelates, it can be seen that the ligands exhibit a C=O stretching band of medium intensity in the region 1698-1735  $\text{cm}^{-1}$  which is observed to be stronger than the usual ketone C=O band (Scheinmann 1970). On chelation with metal the carbonyl absorption peak is shifted to lower frequency (15  $\text{cm}^{-1}$ ) of comparatively low intensity. As there is almost no change in the benzoic carbonyl frequencies on complexation, the benzoic C=O group cannot be considered as a site for coordination. A peak at 1400-1490  $\text{cm}^{-1}$  is due to mixed bend of (C-N) stretch, N-H bend and C=S bend. The strong bands at 3355 to 3400  $\text{cm}^{-1}$  in the case of disubstituted formamido-(N'-substituted) thiocarbamides and carbamides are attributed to N-H stretching of a secondary amine (=NH). In complexes either this peak is

missing or a broad peak covering a range of 3310 to 3350  $\text{cm}^{-1}$  of comparatively low intensity is observed. The infrared spectra of ligands show that BFPTC, BF.o.TTC, BF.p.TTC, DPFPTC, DPF.o.TTC and DPF.p.TTC exhibit a C=S band of the medium intensity 715 to 799  $\text{cm}^{-1}$  which is lowered (11-21  $\text{cm}^{-1}$ ) on complexation.

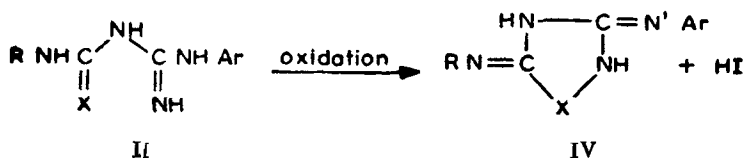
Potentiometric titrations of the ligands indicate that an equal amount of iodine is consumed in the oxidation reaction. It is due to the oxidation of ligands to thiazoles. The interaction of N,N'-diphenyl guanidines or asymmetric guanidines with arylisocyanates and arylisothiocyanates have been shown to afford N,N'-diarylformamidino N'-arylcaramides and thiocaramides(I) and N-benzoylformamidino N'-arylcaramides and thiocaramides(II). The compounds I and II when oxidized undergo ring closure to III and IV, the related 3,5-diaryl-amino-1,2,4-diazolidines and 3,5-diaryl-amino-1,2,4-thiadiazolidines (Dixit 1961).



N,N'-diarylformamidino-N'-arylcaramides,  
thiocaramides

3,5-diaryl-amino-1,2,4-diazolidines and  
thiadiazolidines.

Ph = phenyl ; R = phenyl, orthotolyl, paratolyl ; X = O, S



N-benzoylformamidino N'-arylcaramides,  
thiocaramides.

3,5-diaryl-amino-1,2,4-diazolidines and  
thiadiazolidines.

R =  $\text{C}_6\text{H}_5\text{CO}$  ; Ar = phenyl, orthotolyl, paratolyl ; X = O, S

On titrating the metal complexes with iodine almost constant values of potential are obtained indicating that the complexes are not being oxidized by iodine. This may be due to the fact that the sulphur and oxygen atoms are already bonded to the metal in the metal chloride complexes and are not free to form the thiols. All these observations show that coordination in the case of DPFPTC, DPF.o.TTC, DPF.p.TTC, BFPTC, BF.o.TTC and BF.p.TTC is through sulphur and nitrogen (of the =NH group) while in the case of BFPC and DPFPC complexes the coordination is through oxygen and nitrogen atoms.

### Acknowledgements

The author is thankful to Dr K P Srivastava, Professor of Chemistry, Birla Institute of Technology and Science, Pilani, for providing necessary facilities and to the CSIR, New Delhi, for financial assistance.

**References**

- Akbar Ali M and Livingstone S E 1974 *Coord. Chem. Rev.* **13** 101  
Clarke H T 1960 *A handbook of organic analysis* (London : Advard Arnold) p. 311  
Dixit S N 1961 *J. Indian Chem. Soc.* **38** 221  
Erdey L 1965 *Gravimetric analysis part II* (London : Pergamon) p. 532  
Horsfall J G and Rich S 1951 *Contrib. Boyce Thompson Inst.* **16** 361  
Madhok K L and Srivastava K P 1980 *Indian J. Chem.* **A19** 808  
Mishra H P 1980 Ph.D. thesis (Sambalpur University) p. 6  
Nicholson A R and Sutton G J 1969 *Aust. J. Chem.* **22** 1543  
Srivastava K P and Madhok K L 1978a *Indian J. Chem.* **A16** 359, 990  
Srivastava K P and Madhok K L 1978b *J. Chem. Eng. Data* **23** 256  
Srivastava K P, Srivastava G P, Arya S K and Madhok K L 1980 *J. Chem. Eng. Data* **25**  
173