

**COORDINATION COMPOUNDS OF METAL CHELATES OF SULPHUR
CONTAINING LIGANDS WITH LEWIS BASES**

Reaction of bis(S-methyl-N-arylidenehydrazine carbodithioate)-
nickel(II) Chelates with Pyridine and 1,10-Phenanthroline

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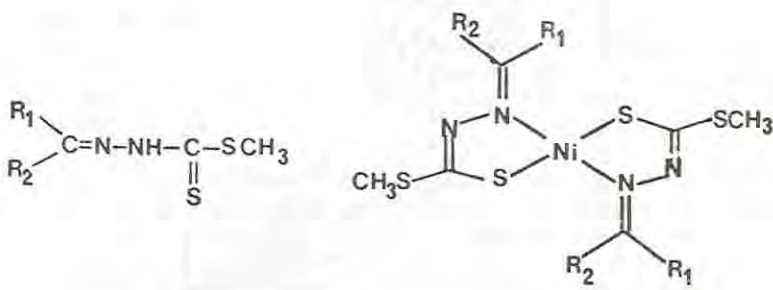
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ABSTRACT: The interaction of the square planar nickel(II) chelates of the type $Ni(R_1R_2C=N-N=CSSCH_3)_2$; NiL_2 derived from ketones [$R_1, R_2=CH_3, CH_3; CH_3, C_2H_5; C_2H_5, C_2H_5; CH_3, CH_2C_6H_5; (CH_2)_5$] with pyridine and 1,10-phenanthroline was studied spectrophotometrically. The stability constants, as well as the thermodynamic parameters ($\Delta G^\circ, \Delta H^\circ, \Delta S^\circ$) for the monoadduct formation reactions were measured. The role of steric factors imposed by the ketonic groups in the parent nickel(II) chelates are emphasized. A distorted pentacoordinate structure was assigned for the pyridine adducts, and a similar structure for the phenanthroline adducts with the exception of the one derived from acetone ($R_1 = R_2 = CH_3$). In the latter case, a distorted octahedral structure was proposed. Stable phenanthroline adducts have been isolated and characterized.

INTRODUCTION

There has been continuing interest in the chemistry of transition metal chelates of schiff bases derived from S-methylhydrazinecarbodithioate(1) (1).

The carcinostatic activity of these chelates(2,3) has attracted particular attention for studying the interaction of these molecules with nitrogen donor



- 1
- R_1
 - CH_3
 - CH_3
 - CH_3
 - CH_2CH_3

- 2
- R_2
 - CH_3
 - CH_2CH_3
 - $CH_2C_6H_5$
 - CH_2CH_3

$(CH_2)_5$

Lewis bases. This may help in understanding their mode of action in biological systems (4-7). The cytotoxic and antitumor activities (2,8) of this class of chelates may result from their binding to the nucleic bases in DNA or other similar targets forming different adducts within the cell.

This paper reports further investigation of the reaction between square planar bis(ligand)nickel(II) chelates of the type (2); NiL_2 , with pyridine (py) and 1,10-phenanthroline (phen).

RESULTS AND DISCUSSION

A series of diamagnetic square planar bis(S-methyl-N-arylidenehydrazine-carbodithioate)nickel(II) chelates, have been synthesized and characterized (9-12). In benzene solution the electronic spectra of these chelates derived from ketones (2) are almost identical and exhibit maximum absorption bands at 365 and 520 nm (12). The addition of a base B (phen or py) to a benzene solution of NiL_2 chelates causes pronounced spectral changes. Typical spectral variations as a function of increasing base concentration are shown in Fig.1. Within the phenanthroline concentration range ($C_{phen}=0.00-9.00 \times 10^{-4} \text{ mol dm}^{-3}$, $C_{NiL_2}=1.00 \times 10^{-4} \text{ mol dm}^{-3}$), the successive absorption curves pass through a sharp isosbestic point at 345 nm. Similar spectral variations were also observed when pyridine was used (12).

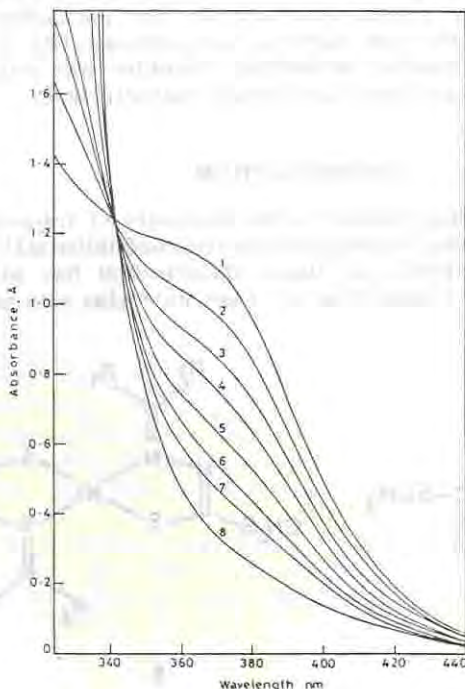
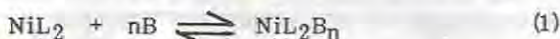


Fig. 1. Spectrophotometric titration of $Ni \left(\begin{array}{c} H_3C \\ | \\ C=N-N=CSSCH_3 \\ | \\ H_5C_2 \end{array} \right)_2$

($1 \times 10^{-4} M$) with 1, 10 - Phenanthroline in benzene solution at $34.1^\circ C$:
 ($C_{phen} \times 10^4 N$): 1) 0.000, 2) 0.300 3) 0.60 4) 0.700,
 5) 1.000, 6) 1.500 7) 2.000 & 8) 9.000.

Analysis of these spectrophotometric titrations in the range 320–440 nm, using the Coleman, Varga and Mastin method(13) confirmed the presence of two light absorbing species in equilibrium, namely the parent square planar nickel(II) chelate (NiL_2), and the base adduct (NiL_2B_n). Such equilibria can be represented by eqn.1, and the adduct formation constant K is given by eqn.2



$$K = \frac{[\text{NiL}_2\text{B}_n]}{[\text{NiL}_2][\text{B}]^n} \quad (2)$$

For computing the formation constants of the highly stable phenanthroline adducts, eqn. 3 was adequately used (14).

$$\frac{A_0 - A}{A - A_\infty} = K [C_{\text{phen}} - n \left(\frac{A_0 - A}{A_0 - A_\infty} \right) C_{\text{NiL}_2}]^n \quad (3)$$

where A_0 , A , A_∞ and n have their usual significance (15,16). For all systems studied, plots of $(A_0 - A / A - A_\infty)$ versus $[C_{\text{phen}} - n (A_0 - A / A_0 - A_\infty) C_{\text{NiL}_2}]^n$ gave straight lines passing through the origin, indicating that $n = 1$. The values of K were evaluated from the gradients of these plots. However, in the case of pyridine, a large excess of the base was used ($C_{\text{py}}/C_{\text{NiL}_2}$ varies from 50 to 1500) to achieve complete adduct formation, and in this case it is assumed that $C_{\text{B}} = [\text{B}]$. The adduct formation constant K can be determined using the logarithmic eqn.4 (13).

$$\text{Log} \frac{A_0 - A}{A - A_\infty} = \text{Log} K + n \text{Log} C_{\text{B}} \quad (4)$$

From the least square linear plots of $\text{Log}(A_0 - A / A - A_\infty)$ vs. $\text{Log} C_{\text{B}}$, the gradient (n) and intercept ($\text{Log} K$) were evaluated, and it was concluded that pentacoordinate monopyridine adducts are formed, with a distorted square pyramidal structure (3a).

The enthalpy (ΔH°) and entropy (ΔS°) changes of the adducts were calculated from plots of $\text{Log} K$ vs $1/T$ over the range 20–40°C. The calculated values of $\text{Log} K$ and the thermodynamic parameters (ΔH° , ΔS° , ΔG°) for all system studied are given in Table 1.

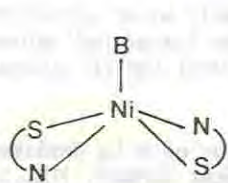
The available results suggest that in benzene the reaction of NiL_2 chelates (2) with pyridine and phenanthroline afforded the monobase adduct; NiL_2B . Also, it is evident from the high and negative values of ΔG° that the phenanthroline adducts are more stable than the corresponding pyridine adducts. The extra stability associated with the phenanthroline adducts could be attributed to the expected bidentate nature of this molecule. Furthermore, the data cited in Table 1, reveals that the values of $-\Delta H^\circ$ for $\text{NiL}_2(\text{Phen})$ adducts are larger than those of the corresponding NiL_2py adducts (except for 2, $R_1, R_2 = (\text{CH}_2)_5$). Since ΔH° is a measure of the bond energy of the reaction, it is reasonable to assume that the phenanthroline adducts exist either in the hexa-, or penta-coordinate structures depending on the nature of the R_1 and R_2 groups, and the extra stability in this series is attributed to entropy

Table 1: Stability Constants and Thermodynamic Parameters for monoadduct of $Ni(R_1R_2C=N-N=CSSCH_3)_2$ with pyridine and 1,10-phenanthroline in benzene at 25°C.

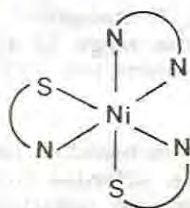
R_1	R_2	Logk	$-\Delta G^\circ$ (kJmol ⁻¹)	$-\Delta H^\circ$ (kJmol ⁻¹)	$-\Delta S^\circ$ (Jmol ⁻¹ K ⁻¹)
i) Phenanthroline adducts:					
CH ₃	CH ₃	4.53	25.8	54.9	97.7
CH ₃	CH ₂ CH ₃	4.54	25.8	42.8	56.9
CH ₃	CH ₂ C ₆ H ₅	5.00	28.4	41.5	44.0
CH ₂ CH ₃	CH ₂ CH ₃	4.56	25.9	49.3	78.5
(CH ₂) ₅		4.14	23.6	30.2	22.3
ii) Pyridine adducts:					
CH ₃	CH ₃ ^a	-0.27	-1.51	29.3	103.4
CH ₃	CH ₂ CH ₃ ^a	0.11	0.63	34.3	113.4
CH ₃	CH ₂ C ₆ H ₅	-0.10	-0.57	24.9	58.6
CH ₂ CH ₃	CH ₂ CH ₃	-0.40	-2.27	17.4	56.9
(CH ₂) ₅ ^a		-0.11	-0.63	31.4	107.6

a) data taken from ref. 12.

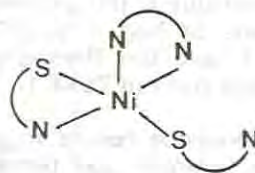
effects. In the case of bis(ligand)nickel(II) chelate derived from acetone (2 , $R_1 = R_2 = CH_3$) the $-\Delta H^\circ$ for the phenanthroline adduct is about twice the corresponding value for the monopyridine adduct, i.e. two Ni-N bonds are formed in the former case, and since $-\Delta S^\circ$ values are close to each other in the two systems, it is reasonable to propose the distorted octahedral structure ($3-b$) for the phenanthroline adduct derived from acetone. However, in case of



3-a



3-b



3-c

cyclohexyl (2 , $R_1, R_2 = C_5H_{10}$) where moderate steric hindrance is introduced by R_1 and R_2 , the values of $-\Delta H^\circ$ for the monopyridine and phenanthroline adducts are almost similar, while ΔS° value of the former adduct is much smaller than the phen adducts. This may be explained by assuming that the parent square planar $NiL_2(2)$ chelate undergoes two Ni-N bond formations with the phen

molecule, and at the same time one Ni-N bond rupture of the hydrazone moiety. The resulting adduct may attain the five coordinate structure (3-c), in which one of the hydrazone molecule behaves as a monodentate ligand through its thiol sulfur, while the other hydrazone retains its bidentate nature. The hanging residue of the monodentate hydrazone molecule is responsible for increasing ΔS° for the phenanthroline adduct over the pyridine one. Such an explanation was presented in studying the reaction of bis(S-methyl-N-arylidenehydrazine-carbodithioate)nickel(II) chelates with 2,2'-bipyridyl in benzene solution (16). Inspection of the rest of the results, in Table 1 reveals that a similar pentacoordinate distorted square pyramidal structure (3-c) could also, be assigned for the phenanthroline adducts (2, $R_1, R_2 = \text{CH}_3, \text{C}_2\text{H}_5; \text{C}_2\text{H}_5, \text{C}_2\text{H}_5; \text{CH}_3, \text{CH}_2\text{C}_6\text{H}_5$) but with different contribution of ΔH° and ΔS° to the reaction depending on the bulkiness of R_1 and R_2 groups. Also, it is interesting to note that when strong steric hindrance is introduced by R_1 and R_2 (2, $R_1, R_2 = \text{CH}_3, \text{C}_6\text{H}_5; \text{C}_6\text{H}_5, \text{C}_6\text{H}_5$) no sign of adduct formation was observed (12). It has been assumed that in case of the monopyridine adduct the addition of the first base molecule results in a considerable downward distortion of the planar NiL_2 chelates, with the nickel atom being above the plane of the N_2S_2 donor atoms, leading to unfavorable attack by the second base molecule (12, 17, 18). The reaction of less sterically hindered NiL_2 chelates derived from aldehydes (2, $R_1, R_2 = \text{H}, \text{C}_6\text{H}_5$) with pyridine affords predominantly octahedral bis adducts (12, 19). The formation of pentacoordinate phen adducts with NiL_2 chelates (where the Ni-N bond has cleaved, 3-c) may be attributed to the combined effects imposed by the strong chelate of the phen molecule and the steric hindrance of R_1 and R_2 groups.

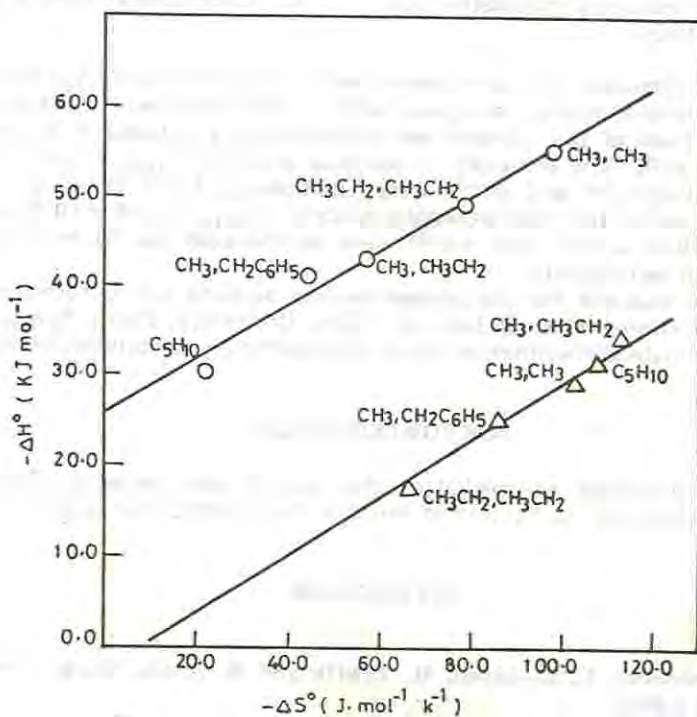


Fig. 2. Variation of the thermodynamic parameters of the mono-adduct formation reaction of $\text{Ni}(\text{R}_1\text{R}_2\text{C}=\text{N}-\text{N}=\text{C}(\text{S}(\text{CH}_3)_2)_2$ with heterocyclic bases: 1) O, 1, 10-phen and 2) Δ , py.

The thermodynamic plots ($-\Delta H^\circ$ vs. $-\Delta S^\circ$) for the monoadduct formation reaction (Fig.2) are linear with an isoequilibrium temperature $\beta = 339^\circ \text{K}$ for pyridine adducts and $\beta = 331^\circ \text{K}$ for phenanthroline adducts (20).

In most cases, the solid pentacoordinate adducts were isolated (21). These adducts are paramagnetic and exhibit moments in the typical range 3.2-3.4 BM, and their solution electronic spectra, in benzene, are in agreement with distorted square pyramidal environment around nickel(II) (12, 22).

EXPERIMENTAL

Materials: Pyridine and 1,10-phenanthroline were of reagent grade and purchased from Merck. Pyridine was distilled over KOH before use, while 1,10-phenanthroline was used without further purification. Benzene was analytical grade, dried and distilled over sodium before use.

Bis(S-methyl-N-arylidenehydrazinecarbodithioate)nickel (II) chelates were prepared and purified as previously described by the reaction of nickel (II) acetate with the appropriate ligand in ethanol (10-12), and crystallized from benzene-petroleum ether (60-80°C).

Preparation of the monophenanthroline adducts: A hot solution of phen (1.7 mmol) in dry benzene (15 ml) was added dropwise to a hot solution of the neutral bis(ligand)nickel(II) chelate in benzene (1.7 mmol in 25 ml). The solution was refluxed for 1/2 hr, then evaporated to half of its volume. On cooling the phenanthroline adduct precipitated out. It was filtered and washed with dry benzene, and ether.

Physical measurements: The electronic spectra were recorded on a Pye Unicam SP 1801 spectrophotometer equipped with a thermostated cell holder. The actual temperature of the solution was measured by a calibrated thermocouple, dipped in the cell. The solutions of pyridine adducts ($C_{NiL_2} = 2.00 \times 10^{-4} \text{ mol dm}^{-3}$, $C_{py} = 0.00-0.30 \text{ mol dm}^{-3}$) were equilibrated for 1 hr at the required temp, while those of the phenanthroline adducts ($C_{NiL_2} = 1.00 \times 10^{-4} \text{ mol dm}^{-3}$, $C_{phen} = 0.00-9.00 \times 10^{-4} \text{ mol dm}^{-3}$) were equilibrated for 24 hr in order for the reactions to be complete.

The nitrogen analysis for the phenanthroline adducts was determined at the elemental and Microanalytical Lab. of Cairo University, Cairo-Egypt, whereas nickel was determined gravimetrically as bis(dimethylglyoximate)nickel(II).

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REFERENCES

1. M. F. Iskander, L. El-Sayed, M. Tawfik and M. Arafa, *Inorg. Chim. Acta*, **104**, 125 (1985).
2. M. Das and S. E. Livingstone, *Brit. J. Cancer*, **37**, 466 (1978).
3. M. Das and S.E. Livingstone, *Inorg. Chim. Acta*, **19**, 5 (1976).

4. D.T. Minkel and D. H. Petering, *Cancer Res.*, **38**, 117 (1978).
5. D.T. Minkel, A. L. Saryan and D. H. Petering, *Cancer Res.*, **38**, 124 (1978).
6. D. T. Minkel, C. H. Chan Stier and D. H. Petering, *Mol Pharmacol.*, **12**, 1036 (1978).
7. C. H. Chan Stier, D. T. Minkel and D. H. Petering, *Bioinorg. Chem.*, **6**, 203 (1976).
8. S. E. Livingstone, 20 th Inter. Conf. Coord. Chem. (1978).
9. M. F. Iskander and L. El-Sayed, *J. Inorg. Nucl. Chem.*, **33**, 4253 (1971).
10. L. El. Sayed, M. F. Iskander, A. El-Toukhy and S. E. Zayan, *Inorg. Chim. Acta*, **6**, 633 (1972).
11. L. El-Sayed, M. F. Iskander and A. El-Toukhy, *J. Inorg. Nucl. Chem.*, **36**, 1739 (1974).
12. M. F. Iskander, M. A. El-Dessouky and S. A. Sallam, *J. Inorg. Nucl. Chem.*, **38**, 2201 (1976).
13. J. S. Coleman, L. P. Varga and S. H. Mastin, *Inorg. Chim. Acta*, **9**, 1015 (1970).
14. M. Cusumano, *J. Chem. Soc. Dalton*, 2133 (1979).
15. M. F. Iskander and S. Saddeck, *Inorg. Chim. Acta*, **22**, 141 (1977).
16. M. F. Iskander, L. El. Sayed, L. Labib and A. El. Toukhy, *Inorg. Chim. Acta*, **86**, 197 (1984).
17. P. S. Shetty and O. Fernando, *J. Am. Chem. Soc.*, **92**, 3964 (1970).
18. J. R. Angus and J. R. Wasson, *J. Coord. Chem.*, **1**, 309 (1971).
19. M. F. Iskander, A. El-Toukhy and M. M. Mishrikey, *J. Inorg. Nucl. Chem.*, **42**, 361 (1980).
20. C. D. Johnson, "The Hammett Equation" Cambridge Univ. Press, London, (1973).
21. Satisfactory elemental analyses were obtained for these adducts.
22. M. F. Iskander, A. El-Toukhy and M. M. Mishrikey, *J. Inorg. Nucl. Chem.*, **42**, 361 (1980).