

Pseudothiohydantoin Complexes of Ni^{II} Halides and Perchlorate

P.P. Singh and U.P. Shukla

Received October 27, 1972

Nickel halide and perchlorate complexes (NiX₂ · 4L). (X = Cl, Br, I, ClO₄ and L = pseudothiohydantoin) have been prepared and characterized. Nickel bromide forms both cis and trans octahedral isomers, whereas other complexes are octahedral with trans configuration. The infrared and electronic spectral studies suggest oxygen as the donor site. Spectral parameter Dq, B', β have also been calculated which suggest a weak ligand field.

Introduction

Pseudothiohydantoin has four centres of coordination, these are exocyclic nitrogen, exocyclic oxygen, ring nitrogen and ring sulphur.

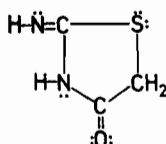


Figure 1.

It is therefore of interest to investigate as to which is the actual site of donation towards metal halide. To investigate this, complexes of nickel(II) halides have been prepared and studied, with the help of infrared and electronic spectra. The infrared results have been correlated with the values of ligand field parameters Dq, B' and β.

Experimental Section

Reagent grade Ni^{II} halides and perchlorate (Alfa Inorganic) were used without further purification. Pseudothiohydantoin (PTHN) was prepared and purified by the method described by Horning.²⁸ Solvents were dried before use, and handling was done in a dry box flushed with nitrogen.

Physical Measurements. Magnetic susceptibility was measured by Gouy method at room temperature. Infrared spectra were recorded on a Perkin-Elmer model 621 spectrophotometer. Solid phase electronic

spectra were obtained on a Beckman model DK-1 recording spectrophotometer using the method outlined by Lee.³³

Preparation of the complexes and analysis. Ni-(PTHN)₄Cl₂ and Ni(PTHN)₄I₂. The complexes were prepared by refluxing and stirring the metal salt and the ligand in 1:4 molar ratio, keeping with a slight excess of metal salt, in ethylene dichloride or acetone for 12 hours. The mass so obtained was filtered. The residue was boiled with ethanol, refiltered, washed with solvent and dried in vacuum.

Ni(PTHN)₄(ClO₄)₂. The nickel perchlorate was stirred with dimethoxy propane for two hours, and to the solution so obtained, a suspension of the ligand in ethylene dichloride was added and refluxed with stirring for 24 hours. The resultant white complex was filtered. The residue was processed as in case of chloride complex, washed with solvent and dried in vacuum.

Ni(PTHN)₄Br₂ (Cis and Trans isomers). Nickel bromide was refluxed and stirred with the ligand in 1:4 molar ratio in ethylene dichloride for 18 hours. A mixture of green and blue mass was obtained, which was filtered washed and dried. This mass was boiled with n-butanol and filtered. The residue was found to be the trans form and from the filtrate cis was crystallised.

Analysis. Halogen and nickel were estimated gravimetrically as silver halides and dimethylglyoximate respectively. Nitrogen was estimated by kjeldahl method. The analytical results are given in Table I.

Results and Discussion

Electronic Spectral Studies. The non conducting nature of the complexes and the values of the magnetic moment Table I, suggest an octahedral configuration for the nickel(II) complexes.^{27,29} As such various band assignments and calculations have been made on the basis of octahedral complexes. The band assignments and the parameters calculated there from are presented in Table II. Dq values of these complexes are in the range of other complexes having oxygen as donor site^{27,29} and the nephelauxetic parameter places this ligand amongst the non π bonding ligands.²⁷

Table I. Analytical Results and Magnetic Susceptibility data.

Complexes	Colour	M.P. (°C)	Metal %		Halogen %		Nitrogen %		Magnetic Susceptibility μ_{eff} (B.M.) (Room Temp.)
			Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	
Ni(PTHN) ₂ Cl ₂	Yellowish green	220(D)	9.78	10.02	11.94	12.12	18.87	19.32	3.18
Ni(PTHN) ₂ Br ₂ (<i>Trans</i>)	Blue	235(D)	8.59	8.97	23.44	23.86	16.41	16.99	3.20
Ni(PTHN) ₂ Br ₂ (<i>Cis</i>)	Green	125	8.59	9.00	23.44	23.95	16.41	16.96	3.20
Ni(PTHN) ₂ I ₂	Light Yellow	150	7.55	8.06	23.70	23.36	14.42	14.70	3.22
Ni(PTHN) ₂ (ClO ₄) ₂	White	165	8.13	8.54	—	—	15.52	15.83	3.14

Table II. Band assignments and spectral parameters of Ni^{II} complexes.

Complexes	${}^3A_{2g} \rightarrow {}^3T_{2g}$ cm ⁻¹	${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ cm ⁻¹	${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ cm ⁻¹	Dq cm ⁻¹	B' cm ⁻¹	β cm ⁻¹	λ' cm ⁻¹
Ni(PTHN) ₂ Cl ₂	9569	15748	27932	956	1000	0.94	296
Ni(PTHN) ₂ Br ₂ (<i>Trans</i>)	9478	15600	27854	947	1002	0.94	307
Ni(PTHN) ₂ Br ₂ (<i>Cis</i>)	9451	15552	27770	945	993	0.94	307
Ni(PTHN) ₂ I ₂	9174	15337	25773	917	906	0.85	298
Ni(PTHN) ₂ (ClO ₄) ₂	9756	15625	27027	975	893	0.84	268

There appears only a little difference in the spectra of *cis* and *trans* complexes of Nickel bromide, hence the values of Dq and β are almost the same for the two. This suggests that change in symmetry of the complexes only slightly affects the electronic transition.

Since the complexes are coloured they can not be believed to be perfectly octahedral. As such the colour may be due to distortion or vibronic coupling as pointed out by Drago.³⁰

Spin orbit coupling. We have calculated effective spin orbit coupling constants (λ') for the Ni^{II} complexes (Table II), these values are about 85-97% of the free ion value (315 cm⁻¹). It shows that there is orbital overlap, resulting in delocalisation of d-electrons. This is concurrent with our Dq and β values.

Characterization of Cis and Trans isomers. Since the blue and green complexes are identical in their analytical data and are different in properties, we consider them as two stereoisomers. These two isomers have been characterized as follows.

The *trans* isomers belongs to D_{4h} and *cis* to C_{2v} point group. Complexes belonging to these point groups will have different number of i.r. active bands (5) as shown in the table below.

Complexes	Point group	Species of Ni-L and Ni-Br stretching modes	Number of i.r. active bands
Cis-NiBr ₂ · 4L	C _{2v}	A ₁ and B ₁	6
Trans-NiBr ₂ · 4L	D _{4h}	B _{2u} or B _{3u}	2

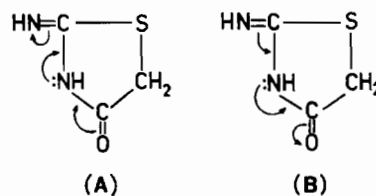
Far i.r. spectra of the green complex show five additional bands (compared to ligand) in the 600-200 cm⁻¹ region. The bands at 275 and 280 cm⁻¹ (Table III), can be attributed to two types of Ni-Br stretching modes⁸ and at 510, 492 and 435 cm⁻¹ to three

types of Ni-L stretching modes.³²

The blue complex has two additional bands, one at 488 cm⁻¹ and the other at 275 cm⁻¹ the former could be attributed to Ni-O and the latter to Ni-Br, stretching modes.^{8,32}

On the basis of the number of bands in the far infrared region we can believe that the green complex has *cis* and the blue has *trans* configuration. The solubility of the green isomer in ethanol and n-butanol and the insolubility of the blue isomer in these solvents further suggests that the green is *cis* and the blue is *trans*.³¹

The *cis* form changes to *trans* form if boiled with a solvent of boiling point about 100°C for at least 4 hours. This lability is perhaps due to weak field interaction of the ligands.

**Figure 2**

Infrared Discussion. The ring NH of PTHN is conjugated with -C=O and -C=NH group. Lone pair electrons of -NH can either polarise towards the nitrogen of the -C=NH (Figure 2A) or towards oxygen of carbonyl (C=O) group (Figure 2B).

Table III. Assignments of infrared bands in the ligand and the complexes in nujol.

Ligand=L (cm^{-1})	$\text{NiCl}_2 \cdot 4\text{L}$ (cm^{-1})	$\text{NiBr}_2 \cdot 4\text{L}$ (<i>cis</i>) cm^{-1}	$\text{NiBr}_2 \cdot 4\text{L}$ (<i>trans</i>) cm^{-1}	$\text{NiI}_2 \cdot 4\text{L}$ cm^{-1}	$\text{Ni}(\text{ClO}_4)_2 \cdot 4\text{L}$ cm^{-1}	Assignments Ref. 1-8
3375(ms)	3260(mb)	3230(b)	3280(b)	5300(b)	3330(m)	(N-H) st.
3220(mb)	3110(mb)	—	3200(b)	3210(wb)	3220(mb)	(=N-H) st.
1725(s)	1605(sb)	1600(sb)	1600(mb)	1605(mb)	—	(C=O) st.
1650(s)	1650(mb)	1650(b)	1655(s)	1650(mb)	1640(sb)	(N-H) def.
1510(ms)	1500(mb)	1500(b)	1500(m)	1500(m)	1510(s)	(C=N) st.
1370(m)	1395(m)	1395(ms)	—	1390(m)	1390(ms)	(C-N) st.
700(s)	700(s)	705(ms)	700(m)	700(ms)	700(m)	(C-S) st.
—	510(w)	510(m)	488(ms)	480(s)	480(s)	(M-O) st.
—	—	492(m)	—	—	—	(M-L) st.
—	—	435(w)	—	—	—	(M-L) st.
—	—	280(m)	—	—	—	(M-Br) st.
—	—	275(ms)	275(ms)	—	—	(M-Br) st.
—	350(ms)	—	—	—	—	(M-Cl) st.

m = medium, s = strong, b = broad, w = weak, mb = medium broad, ms = medium strong, wb = weak, broad sb = strong broad.

Table IV. Observed shifts in i.r. absorption frequencies, cm^{-1} .

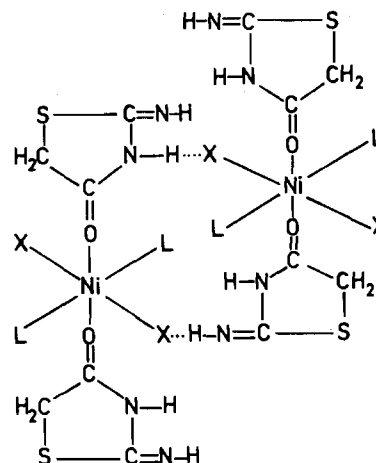
Complexes	(N-H)	(=N-H)	(C=O)	(C-N)	(C=N)
$\text{Ni}(\text{PTHN})_2\text{Br}_2$	-115	-110	-120	+25	-10
$\text{Ni}(\text{PTHN})_2\text{Cl}_2$ (<i>cis</i>)	-145	—	-125	+25	-10
$\text{Ni}(\text{PTHN})_2\text{Br}_2$ (<i>trans</i>)	-95	-20	-125	—	-10
$\text{Ni}(\text{PTHN})_2\text{I}_2$	-75	-10	-120	+20	-10
$\text{Ni}(\text{PTHN})_2(\text{ClO}_4)_2$	-45	—	—	+20	—

Thus, nitrogen of $-\text{C}=\text{NH}$ and oxygen of $-\text{C}=\text{O}$ group are almost in equally comfortable position to coordinate with the metal atom. If coordination occurs through the exocyclic nitrogen, the $\text{C}=\text{N}$ and $\text{N}-\text{H}$ stretching frequencies should decrease.¹⁵ Coordination through the carbonyl oxygen on the other hand will result in decrease of $\text{C}=\text{O}$ stretching frequency and increase in $\text{C}-\text{N}$ stretching frequency.^{16,17,18} The results of our infrared study show a negative shift of the order -125 cm^{-1} in $\text{C}=\text{O}$ stretching frequency and a positive shift of the order $+25 \text{ cm}^{-1}$ in the $\text{C}-\text{N}$ stretching frequency, Table IV, suggesting coordination through the carbonyl oxygen.^{9,16}

We also observe, in our complexes, a negative shift of the order -115 cm^{-1} , -100 cm^{-1} and -10 cm^{-1} , (Table IV), in the $\text{N}-\text{H}$, $=\text{N}-\text{H}$ and $\text{C}=\text{N}$ stretching bands respectively. These shifts may be due to: (a) coordination through either of the two imino nitrogens^{21,22} (b) hydrogen bonding between imino hydrogen and halogen of the metal halide.^{23,24} Shifts in the $\text{C}=\text{O}$ and $\text{C}-\text{N}$ stretching bands do not support the first possibility. Thus hydrogen bonding may be the reason of negative shift. This hydrogen bonding may be intramolecular or intermolecular.

To examine this, we constructed a molecular model and found that hydrogen of $\text{N}-\text{H}$ is about 4 Å away from the halogens. For the intramolecular hydrogen bonding atoms should not be far apart than 3 Å.²⁵ Thus the hydrogen bonding is intermolecular and not intramolecular as shown in figure below.

PTHN has four coordinating sites but it coordinates through oxygen. Let us see as to why the oxygen atom is the preferential donor site in compari-

**Figure 3.**

son to other donor atoms. The presence of two electronegative groups adjacent to ring nitrogen makes it less favourable for coordination. On the other hand the polarisation of lone pair electrons of the ring nitrogen will be more towards oxygen than the exocyclic nitrogen due to higher electronegativity of oxygen. Hence carbonyl oxygen will have greater tendency to coordinate with the metal ion. As regards sulphur, it is least electronegative as compared to other donor atoms (N,O). Furthermore electromeric and inductive effects do not favour the accumulation of electrons on sulphur atom, hence it can also not be the donor site.

While discussing electronic spectra we had pointed out that the Dq and β values of pseudothiohydantoin are almost similar to other oxygen bonding ligands. The i.r. results also suggest bonding through oxygen. Thus the two results are concurrent.

We can thus conclude that whenever N-H group is conjugated with two electronegative groups like C=N and C=O, the carbonyl oxygen will be the preferred site of bonding.

M-O and M-X bands. The bands at 510 cm^{-1} , 480 cm^{-1} and 480 cm^{-1} (Table III) are assigned to M-O and at 350 cm^{-1} to Ni-Cl stretching frequencies. These assignments are in agreement to the previous work.^{5,32} Ni-I band could not be observed as it was expected to appear below 200 cm^{-1} . The far i.r. spectra of the chloride, iodide and perchlorate complexes are similar to the spectrum of *trans* isomer, hence these complexes will also have *trans* configuration.

Conclusions

1. The *cis* and *trans* forms have only a little difference in their electronic spectra, hence in their Dq and β values.

2. Only NiBr₂ forms *cis* and *trans* isomers with PTHN.

3. When N-H group is conjugated with two electronegative groups eg. C=N and C=O, carbonyl oxygen will be the preferred site of bonding.

Acknowledgement. The authors wish to thank authorities of M.L.K. College, Balrampur for providing research facilities, to CIDA-NRC for providing senior fellowship to one of us (PPS) who carried instrumen-

tation at University of Montreal, and to UGC New-Delhi for providing financial assistance.

- (1) C.N.R. Rao, R. Vankatravan, and T.R. Kasturi, *Can. J. Chem.*, **42**, 36 (1964).
- (2) L.J. Bellamy, *The Infrared Spectra of Complex Molecules*, p. 270, Methuen London (1958).
- (3) A.R. Katrizky and R.A. Jones, *J. Chem. Soc.*, 497 (1950).
- (4) D. Hadzi, *J. Chem. Soc.*, 847 (1959).
- (5) M. Sckizaki and K. Yamasaki, *Rev. Chim. Minerale*, **6**, 255 (1969).
- (6) S.C. Jain and R. Rivest, *Inorg. Chim. Acta*, **3**, 552 (1969).
- (7) K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, p. 217, John Wiley, New York (1963).
- (8) J.R. Ferraro, *Low Frequency Vibrations of Inorganic and Coordination Compounds*, p. 140, Plenum Press, New York (1971).
- (9) S.K. Madan and J.A. Sturr, *J. Inorg. Nucl. Chem.*, **29**, 1969 (1967).
- (10) S.K. Madan and M. Sulich, *Inorg. Chem.*, **5**, 1062 (1966).
- (11) M. Nardelli, I. Chierici, and A. Braibanti, *Gazz. Chim. Ital.*, **88**, 37 (1958).
- (12) R.L. Carlin and S.L. Holt, *Inorg. Chem.*, **2**, 849 (1963).
- (13) S.L. Holt Jr. and R.L. Carlin, *J. Am. Chem. Soc.*, **86**, 5017 (1964).
- (14) D.M. Adams and J.B. Cornell, *J. Chem. Soc. (A)*, 884 (1967).
- (15) S.C. Jain and R. Rivest, *J. Inorg. Nucl. Chem.*, **29**, 2787 (1967).
- (16) P.P. Singh and I.M. Pandey, *J. Inorg. Nucl. Chem.*, **34**, 591 (1972).
- (17) R.C. Aggarwal and P.P. Singh, *Z. Anorg. Allg. Chem.*, **332**, 105 (1964).
- (18) R.B. Penland, S. Mizushima, C. Curran, and J.V. Quagliano, *J. Am. Chem. Soc.*, **79**, 1575 (1957).
- (19) T. Miyazawa, T. Shimanouchi, and S.I. Mizushima, *J. Chem. Phys.*, **19**, 611 (1958).
- (20) T. Archambault and R. Rivest, *Can. J. Chem.*, **38**, 1331 (1960).
- (21) N.N. Greenwood and B.H. Robinson, *J. Chem. Soc. (A)*, 512 (1967).
- (22) S.C. Jain and R. Rivest, *Can. J. Chem.*, **45**, 159 (1967).
- (23) I. Chatt, L.A. Duncanson, and L.M. Venanzi, *J. Chem. Soc.*, 2712 (1956).
- (24) A. Nakahara, Y. Saito, and H. Kuroya, *Bull. Chem. Soc. Japan*, **25**, 331 (1962).
- (25) J.C.P. Schwarz, *Physical Methods in Organic Chemistry*, p. 68, Oliver and Boyd Edinburgh-1 (1964).
- (26) C.W.A. Fowles, R.W. Mathews, and R.A. Walton, *J. Chem. Soc. (A)*, 1108 (1968).
- (27) A. Kleinstein and G.A. Webb, *J. Inorg. Nucl. Chem.*, **33**, 405 (1971).
- (28) E.C. Horning, *Organic Synthesis* vol. 3, p. 751, John Wiley, New York (1962).
- (29) A.B.P. Lever and D. Ogden, *J. Chem. Soc. (A)*, 2041 (1967).
- (30) R.S. Drago, *Physical Methods in Inorganic Chemistry*, p. 161, Reinhold, New York (1968).
- (31) Jeffrey J. Sirola and R.O. Ragsdale, *Inorg. Chem.*, **4**, 760 (1965).
- (32) S.H.H. Chaston, S.E. Livingstone, T.N. Lockyer, V.A. Pickles, and J.S. Shannon, *Aust. J. Chem.*, **18**, 673 (1965).
- (33) R.H. Lee, G. Griswold, and J. Kleinberg, *Inorg. Chem.*, **3**, 1278 (1964).