Indian Journal of Chemistry
Vol. 14A, March 1976, pp. 166-169

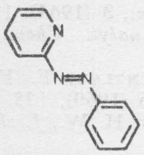
Structure of Complexes of 2-Phenylazopyridine with Perchlorate Halides of Ni(II) & with Ferrous Iodide

B. S. RAGHAVENDRA & A. CHAKRAVORTY*
Department of Chemistry, Indian Institute of Technology, Kanpur 208016

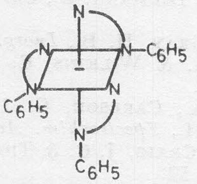
Received 9 October 1975; accepted 19 November 1975

2-Phenylazopyridine (L) acts as an unsymmetrical bidentate chelating ligand. The tris species NiL_3^{2+} and FeL_3^{2+} are isolated in the form of perchlorate and iodide respectively. The complex cations are pseudooctahedral presumably with a meridional *trans* structure. From the ligand field spectrum of paramagnetic NiL_3^{2+}, *Dq* of L is calculated to be 1080 cm^{-1}, a value which is close to that for ethylenediamine in $Nien_3^{2+}$ but is considerably less than that of chelating diimines, such as pyridinalimine. The isoelectronic relationship between the diimine and azoamine fragments is noted. FeL_3^{2+} shows an intense band in the visible region which is assigned to electron transfer from metal t_{2g} (idealized O_h) to ligand π* orbital. That the charge transfer state has contribution to the ground state also is evident from IR data. The N = N stretch is considerable lowered in FeL_3^{2+} in comparison to those in the ligand and in Ni(II) complexes. The paramagnetic complexes NiL_2X_2, 0·5 CH_2Cl_2 (X = Cl, Br) and diamagnetic NiL_2I_2 are reported. On the basis of magnetic, electrical conductivity and electronic spectral data, it is suggested that NiL_2X_2, 0·5 CH_2Cl_2 has pseudooctahedral Ni(II) (X in *cis* positions) with dichloromethane held in the crystal lattice but not influencing the Ni(II) environment in any major manner. In NiL_2I_2 the two ligands are believed to be held in a *trans* planar manner. Iodide ions may be providing weak axial coordination. Major bands in the IR spectra of the various complexes are assigned.

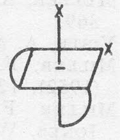
An azo group suitably linked to an aromatic ring carrying additional donor sites is well suited for closure of a chelate ring. Good examples of such a situation are provided by the metal complexes of arylazophenols whose chelating activity has been known for many years[1-3]. A phenyl azo group attached to the 2-position of a pyridine ring as in 2-phenylazopyridine (1) may be expected to give stable metal chelates. This problem is explored for the first time in the present paper. Some related studies recently reported in literature are those on more complicated systems such as 2,2′-, 3,3′- and 4,4′-azopyridines[4-6].



1



2



3

Materials and Methods

2-Phenylazopyridine was prepared in relatively poor yield by condensing 2-aminopyridine with nitrosobenzene according to the literature[7] procedure.

$NiL_3(ClO_4)_2$— A solution of $Ni(ClO_4)_2.6H_2O$ (0·001 mole) in methanol was added to a solution of the ligand (0·003 mole) in the same solvent. The colour of the reaction mixture was dark green. The mixture was kept overnight at room temperature. The dark green crystals formed were filtered, washed with little methanol and dried (5 mm, 80°).

FeL_3I_2— An aq. ethanolic solution containing $FeSO_4$. $7H_2O$ (0·001 mole) and ligand (0·003 mole) was warmed and to this concentrated potassium iodide solution was added. On cooling to 5°, violet crystals were deposited. These were recrystallized from water containing dissolved potassium iodide.

$NiL_2Cl_2.0{\cdot}5CH_2Cl_2$— A methanolic solution of $NiCl_2.6H_2O$ (0·001 mole) was added to a methanolic solution of the ligand (0·002 mole). The solvent was removed by heating on a steam-bath resulting in a gum which was then extracted with dichloromethane. The extract was concentrated and cooled to room temperature. A dark coloured crystalline solid (green when powdered) deposited which was further recrystallized from dichloromethane. The crystals analysed as $NiL_2Cl_2{\cdot}0.5CH_2Cl_2$. The bromo compound was similarly prepared starting from $NiBr_2$.

NiL_2I_2— A methanolic solution containing $Ni(CH_3COO)_2.4H_2O$ (0·001 mole) and ligand (0·002 mole) was gently warmed. Potassium iodide solution was then added to this mixture. The dark solid thus obtained yields dark crystals (brown when powdered) on recrystallization from chloroform-hexane mixture.

Physical measurements — Infrared spectra were recorded on a Perkin-Elmer 521 recording spectrophotometer. Electronic spectra were studied on a Cary-14 recording spectrophotometer. Magnetic moments were measured using a sensitive Guoy

---

*To whom all correspondence should be addressed.

TABLE 1 — CAHRACTERIZATION DATA

Compound	C (%)		N (%)		Metal (%)	
	Calc.	Found	Calc.	Found	Calc.	Found
FeL_3I_2	46·10	46·35	14·66	14·79	6·50	6·45
$NiL_3(ClO_4)_2$	49·00	49·28	15·60	15·80	7·27	7·10
$NiL_2.0{\cdot}5CH_2Cl_2$(a)	48·70	48·43	15·49	15·24	10·82	10·60
$NiL_2Br_2.0{\cdot}5CH_2Cl_2$(b)	42·47	42·26	13·04	13·15	9·11	9·23
NiL_2I_2	38·88	38·43	12·37	12·43	8·65	8·84

(a) The percentage of chloride directly bound to nickel (Calc. 13·07; found 12·72%).
(b) The percentage of bromide directly bound to nickel (Calc. 24·80; found 24·90%).

TABLE 2 — ELECTRICAL CONDUCTIVITY(a) AND MAGNETIC SUSCEPTIBILITY DATA

Compound	Temp. (°C)	Λ_M (ohm^{-1} cm^2 mole^{-1})	Temp. (°C)	μ_{eff} (B.M.)
$NiL_3(ClO_4)_2$	25	175	28	3·12
FeL_3I_2	19	141	26	Diamagnetic
$NiL_2Cl_2.0{\cdot}5CH_2Cl_2$	19	9	22	3·05
$NiL_2Br_2.0{\cdot}5CH_2Cl_2$	19	16	22	3·10
NiL_2I_2	20	45	22	Diamagnetic

(a) In $10^{-3}M$ nitromethane solution.

balance described elsewhere[8]. Electrical conductivity measurements were done in nitromethane solution using a Systronics conductivity bridge.

Results and Discussion

The ligand (1, abbrev. as L) readily reacts with Ni(II) salts yielding complexes of the type $NiL_3(ClO_4)_2$, $NiL_2X_2.0{\cdot}5CH_2Cl_2$ (X=Cl, Br) and NiL_2I_2. In the crystalline state $NiL_3(ClO_4)_2$ is green while the other species are very dark coloured. In dichloromethane or chloroform solution the respective colours are: $NiL_3(ClO_4)_2$, green; NiL_2X_2,0·5 CH_2Cl_2, brownish green and NiL_2I_2, brown. The dark coloured crystals of FeL_3I_2 obtained by direct reaction between ferrous sulphate heptahydrate and the ligand (followed by the addition of potassium iodide) readily dissolve in water to yield deep blue solutions which are not very stable. Analytical data for all complexes are set out in Table 1. Electrical conductivity (in nitromethane solution) and magnetic data are displayed in Table 2. Some characteristic infrared frequencies are shown in Table 3, while electronic spectral data are presented in Table 4.

Structure of tris complexes — Electrical conductivity data (Table 2) for both $NiL_3(ClO_4)_2$ and FeL_3I_2 falls within the range[9] expected for 1: 2 electrolytes. Clearly the complex cation ML_3^{2+} is present in these species.

$NiL_3(ClO_4)_2$ is fully paramagnetic (Table 2). In the electronic spectrum three bands in the visible region (Fig. 1a) establish a gross octahedral geometry for the cation NiL_3^{2+}. In idealized O_h symmetry the bands are readily assigned as $^3A_{2g} \rightarrow {}^3T_{2g}(F)$, 10800 cm^{-1}; $\rightarrow {}^1E(D)$, 11900 cm^{-1} and $\rightarrow {}^3T_{1g}(F)$, 16400 cm^{-1}. The $^3A_2 \rightarrow {}^3T_{1g}(P)$ transition is hidden under intense absorption in the UV. The *Dq* value of L is thus 1080 cm^{-1}, which is considerably lower than that of isoelectronic 2-pyridinalimine species ($Dq \sim 1250$ cm^{-1}) but is close to that of en in $Nien_3^{2+}$ (en = ethylenediamine)[10]. Since L is an unsymmetrical bidentate ligand, NiL_3^{2+} can exist[11] in two isomeric forms, *cis* and *trans*. In the *cis* form the three phenyl groups are crowded on one face of the octahedron while in the *trans* form these are meridionally disposed. In such a situation the *trans* form is usually of much greater stability[11]. We propose that NiL_3^{2+} has the *trans* structure (2).

FeL_3I_2 is diamagnetic at room temperature. The metal atom thus has a low-spin d^6 configuration. It is logical to assume that FeL_3^{2+} also has the *trans* structure (2). The most characteristic feature of the electronic spectrum of FeL_3I_2 (Fig. 1b) is an intense band in the visible region near 16900 cm^{-1}; there is a shoulder at slightly higher energy (18200 cm^{-1}). It is well known that tris-diimine complexes of Fe(II) show an allowed charge transfer transition from metal t_{2g} orbital (idealized O_h) to the lowest empty diimine π^* orbital[12-15]. This transition is seen in the form of a band at ~18000 cm^{-1} associated with a shoulder at slightly lower energies. The shoulder is believed to be the first member in a vibrational progression (coupling with $C\overset{\dots}{-}C + C\overset{\dots}{-}N$ vibrations). The azoimine group $-N=N-C=N-$ is isoelectronic with the diimine function $-N=C-C=N-$ as we have noted earlier[16]. Consequently low energy metal-to-ligand charge transfer transition may be expected in FeL_3^{2+} also. Indeed the 17000 cm^{-1} band in the latter complex is undoubtedly due to such a transition. We note that the metal-to-ligand transition in FeL_3^{2+} is at considerably lower energy than that in $Fe(diimine)_3^{2+}$. FeL_3^{2+} also shows a band at 26500 cm^{-1}. The origin of this band is not certain; the ligand itself has absorption in this region (Table 4).

The $-N=N-$ stretching frequencies in the ligand and Ni(II) complex occur in the narrow range 1418-1431 cm^{-1} (Table 3) as expected[4,17]. On the other hand, there is a dramatic decrease of this frequency to 1353 cm^{-1} in FeL_3^{2+}. This is evidently due to some contribution of the metal-to-ligand charge transfer state to the ground level as in the case of $Fe(diimine)_3^{2+}$ species[12-15] ($C\overset{\dots}{-}N$ stretch is lowered).

Structure of $NiL_2X_2{\cdot}0{\cdot}5CH_2Cl_2$(X=Cl, Br)— These two compounds are fully paramagnetic in the solid

TABLE 3(a) — SELECTED INFRARED FREQUENCIES (cm^{-1})

Assignment	L	FeL_3I_2	$NiL_3(ClO_4)_2$(b)	$NiL_2Cl_2 \cdot 0{\cdot}5CH_2Cl_2$(c)	$NiL_2Br_2 \cdot 0{\cdot}5CH_2Cl_2$(c)	NiL_2I_2
Aromatic	1616 (s)	1599 (s)	1605 (s)	1605 (s)	1604 (s)	1600 (s)
C = C and C = N	1587 (m)	1579 (m)	1586 (m)	1587 (m)	1587 (m)	1582 (m)
	1477 (m)	1458 (m)	1474 (m)	1472 (m)	1468 (m)	1468 (m)
	1456 (s)	1446 (s)	1446 (m)	1452 (s)	1446 (s)	1447 (s)
N = N	1425 (s)	1353 (s)	1428 (s)	1431 (s)	1426 (s)	1418 (s)
C-H out-of-plane bending in phenyl ring	687 (s)	692 (s)	691 (s)	698 (s)	692 (s)	692 (s)
C-H out-of-plane bending in pyridine ring	784 (s)	772 (s)	770 (s)	773 (s)	765 (s)	770 (s)

(a) An unassigned band of medium intensity appears in the range 740-750 cm^{-1} in all compounds studies. (b) ν_3 of ClO_4 is observed as a broad band of high intensity centred at 1100 cm^{-1}. (c) C-Cl stretch of CH_2Cl_2 is at 726 cm^{-1} (m).

TABLE 4 — FREQUENCIES (ν, cm^{-1}) AND EXTINCTION COEFFICIENTS (ϵ, litre mole^{-1}) OF SOME ELECTRONIC BANDS

Compound*	Medium	ν (ϵ)
FeL_3I_2	Solution (water)	16900 (5150); 18200 (3850) sh; 26320 (16900) sh; 31250 (37800)
$NiL_3(ClO_4)_2$	Solution (dichloromethane)	10900 (12); 11700 (15) sh; 16400 (355); 30770 (38130)
$NiL_2Cl_2.0{\cdot}5CH_2Cl_2$	Solution (chloroform)	8630 (13); 16500 (122) sh; 22470 (510); 31250 (2390)
	Solid	9450; 16400 sh; 23200
$NiL_2Br_2.0{\cdot}5CH_2Cl_2$	Solution (chloroform)	8700 (16); 17000 (202) sh; 22730 (1240) sh; 29160 (2825)
	Solid	9350; 16250 sh; 24400 sh

*Ligand (L) shows bands at 22370 and 29410 cm^{-1}.

state (Table 2). The molar electrical conductivities of 1: 1 electrolytes in nitromethane lie[9] in the range 75-95 ohm^{-1}cm^2 mole^{-1}. The observed conductivities of the present complexes show that they are only slightly dissociated in solution (Table 2). The dichloromethane of crystallization is strongly held in the lattice and is not removed even at low pressure (5 mm) and elevated temperature (80°). Quite a few transition metal complexes which contain dichloromethane of crystallization are now known[18]. We wish to stress that the present compounds can also be prepared as amorphous powders without the dichloromethane of crystallization. On the other hand, well-formed crystals which are easy to purify are obtained when dichloromethane is present. The solid state IR spectra of NiL_2Br_2 and $NiL_2.Br_2 \cdot 0{\cdot}5CH_2Cl_2$ were found to be essentially superimposable except that the latter compound shows bands characteristic of dichloromethane also. The dichloromethane of crystallization does not appear to affect the ligand disposition in any major way.

Considerable interest has been shown in recent years about the stereochemistry of complexes of the type NiB_2X_2 where B is a bidentate ligand. There is evidence[19] that when X is widely separated from B in the spectrochemical series, the *cis* configuration is preferred over the *trans* structure. Good examples are $Ni(phen)_2X_2$ (ref. 19), $Ni(en)_2X_2$ (dimer) (ref. 20) and $Ni(po)X_2$ (ref. 21) where phen = *o*-phenanthroline, en = ethylenediamine, po = 2-pyridinaloxime and X = Cl, Br, I. In going from NiN_6 to *trans*-NiN_4X_2, the octahedral $^3A_{2g} \rightarrow {}^3T_{2g}$ (ν_1) band shows observable splitting due to decrease of symmetry from O_h to D_4. A good example is *trans*-$Ni(Py)_4Br_2$ (ref. 21, 22). The *cis*-NiN_4X_2 sphere has lower symmetry (C_{2v}) than *trans*-NiN_4X_2

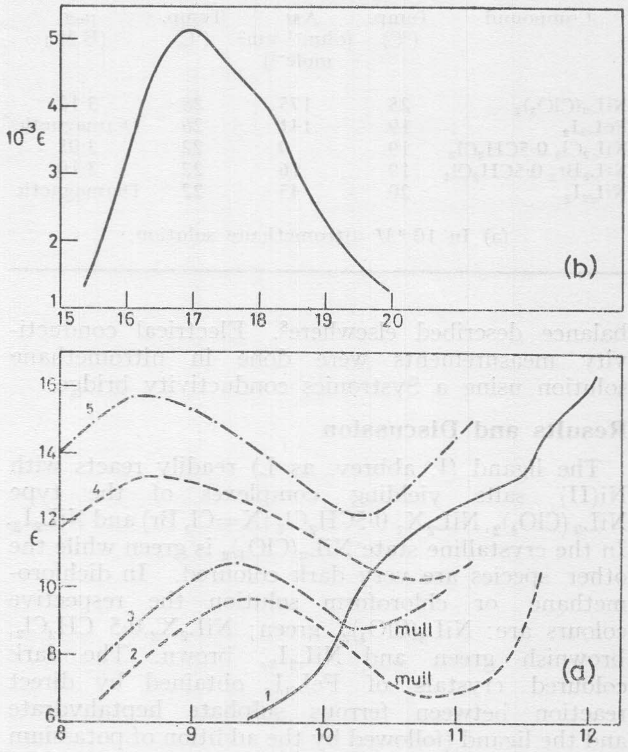


Fig. 1 — Electronic spectra of the complexes [(a): (1) $NiL_3(ClO_4)_2$ in CH_2Cl_2; (2) and (4) $NiL_2Cl_2,0{\cdot}5CH_2Cl_2$ in nujol mull and $CHCl_3$ respectively; (3) and (5) $NiL_2Br_2,0{\cdot}5CH_2Cl_2$ in nujol mull and $CHCl_3$ respectively; in the case of nujol mull the absorption coefficient axis is in arbitrary units. (b) FeL_3I_2 in water]

but the magnitude of orbital splitting is expected to be less[23]. In practice such splitting is often not observed[19,21]. The complexes of 2-phenylazopyridine under discussion shows an unsplit ν_1 band at 9400 cm^{-1} (solid) or at 8600 cm^{-1} (solution) (Fig. 1). Previously we have noted that 2-phenylazopyridine and ethylenediamine have similar ligand field strengths. In this context it is significant that ν_1 of solid Nien$_2$Cl$_2$(dimer) is at 10200 cm^{-1} (ref. 21), a value which is very close to that of the presently synthesized NiL_2Cl_2. However, NiL_2Cl_2 unlike the ethylenediamine complex cannot be dimeric, i.e. $L_2NiCl_2NiL_2Cl_2$, in view of the electrical conductivity data (*vide supra*). On the basis of above discussion we propose that NiL_2X_2 has the structure (3).

NiL_2I_2— This is diamagnetic and shows no ligand field bands below 16000 cm^{-1}. In this complex the NiL_2 sphere is evidently grossly planar presumably with a *trans* (steric overcrowding of phenyl group in *cis* geometry) disposition of ligand molecules. The iodide ions remain partially bound in solution, since the observed electrical condutivity is much lower than that expected for a 1: 2 electrolyte. In view of the proposed difference in stereochemistry of the NiL_2 fragment in the chloro (bromo), and iodo complexes, it may be significant that the N=N stretch in former (no centre of symmetry) is considerably more intense than that of the latter (centre of symmetry).

Acknowledgement

The financial support provided by the CSIR, New Delhi, and the Department of Atomic Energy, Government of India, are gratefully acknowledged.

References

1. Elkins, M. & Hunter, L., *J. chem. Soc.*, (1935), 1598.
2. Pfeiffer, P., Hesse, Th., Pfitzinger, H., Scholl. W & Thielert, H., *Z. prakt. Chem.*, **109** (1937), 217.
3. Chakravorty, A. & Kalia, K. C., *Inorg. Chim. Acta*, **2** (1968), 154.
4. Baldwin, D. A., Lever, A. B. P. & Parish, R. V., *Inorg. Chem.*, **8** (1969), 107.
5. Beadle, P. J., Goodgame, D. M. L., Goldstein, M. & Grazeskowiak, R., *Inorg. Chem.*, **8** (1969), 1490.
6. Beadle, P. J. & Grazeskowiak, R., *J. chem. Soc.*, (A) (1970), 305.
7. Campbell, N., Henderson, A. W. & Taylor, D., *J. chem. Soc.*, (1953), 1281.
8. Kannan, T. S. & Chakravorty, A., *Inorg. Chem.*, **9** (1970), 1153.
9. Geary, W. J., *Coord. Chem. Rev.*, **7** (1971), 81.
10. Rabinson, M. A., Curry, J. D. & Busch, D. H., *Inorg. Chem.*, **2** (1963), 1178.
11. Chakravorty, A. & Kalia, K. C., *Inorg. Chem.*, **7** (1968), 2016.
12. Krumholz, P., *Structure and bonding*, **9** (1971), 139.
13. Sanders, N., *J. chem. Soc.* (A) (1971), 1563.
14. Ito, T., Tanaka, N., Hanazaki, I. & Nagakura, *Bull. chem. Soc. Japan*, **41** (1968), 365.
15. Krumholz, P., *Inorg. Chem.*, **4** (1965), 612.
16. Gupta, S. & Chakravorty, A., *Inorg. Nucl. Chem. Lett.*, **9** (1973), 109.
17. Bassignana, P. & Cogrossi, C., *Tetrahedron*, **20** (1964), 2361.
18. Addision, A. W. & Gillard, R. D., *J. chem. Soc.* (A), (1973), 2002.
19. McKenzie, E. D., *Coord. Chem. Rev.*, **6** (1971), 187.
20. Porai-Koshits, M. A., Shrelashvili, A. E., Antsyshkina, A. S. & Minacheva, L. Kh., *Russ. J. Inorg. Chem.*, **13** (1968), 651.
21. Lees, G., Holmes, F., Underhill, A. E. & Powell, D. B., *J. chem. Soc.* (A) (1971), 337.
22. Sacconi, L., *Transition metal Chem.*, **4** (1968), 199.
23. Yamatera, H., *Bull. chem. Soc. Japan*, **31** (1958), 95; McClure, D. S., *Advances in the chemistry of coordination compounds* (McMillian, New York), 1961, 498.