Inorganica Chimica Acta, *181* (1991) 269–272

Anionic complexes of nickelate(II): coordination number four, five and six

Minati Baral, B. K. Kanungo* and B. Pradhan**

Department of Chemistry, Regional Engineering College, Rourkela - 769 008 (India)

(Received April 18, 1990; revised October 17, 1990)

Abstract

A series of complexes of the types $[Me_4N][Ni(AA)Cl_2]$ and $[n\text{-cepy}][NiCl_3L]$, where Me_4N = tetramethylammonium ion, n-cepy = n-cetylpyridinium ion; AA = pyridyl-2-aldoxime (pyao), acetylacetone (acac), 2-mercapto benzothiozole (mbt); L = γ-picoline (γ-pic), pyridine-*N*-oxide (pyNO) and 4-cyanopyridine-*N*-oxide (4-CNpyNO), and $[Me_4N][Ni(et_2dtc)_2Cl]$ and $[Me_4N][Ni(OX)_3]$, was prepared. The complexes were studied through elemental analyses, molecular weight, molar conductance, magnetic susceptibility, infrared and electronic spectral data. All the complexes are 1:1 electrolytes and tetrahedral, except $[Me_4N][Ni(et_2dtc)_2Cl]$ and $[Me_4N][Ni(OX)_3]$ which are trigonal bipyramidal and octahedral, respectively.

Introduction

For nickel(II), a large number of complexes with coordination number 4, 5 and 6 are known. Among the four coordinated ones complexes of the type $[NiX_4]^{2-}$ have been isolated with different cations [1]. The study of mixed ligand complexes have generated considerable interest among the coordination chemists due to their biological importance in the living system and a large number of ternary metal complexes have been reported by several workers [2, 3]. The chelates acetylacetone, pyridyl-2-aldoxime, 2-mercaptobenzothiozole, diethyldithiocarbamate and 8-hydroxyquinoline, and ligands such as γ-picoline, pyridine-*N*-oxide and 4-cyano-pyridine-*N*-oxide have been well studied [4–12]. In continuation of the previous work [13] on mixed ligand complexes and keeping the above facts in view, an attempt has been made to react $[NiX_4]^{-2}$ with different monodentate and bidentate ligands of biological importance and in the presence of suitable cations such as tetramethylammonium and n-cetylpyridinium ions; a series of mixed ligand complexes has been synthesized by replacement of one, two or all of the chloride ions. Though the reactions were aimed at isolating complexes with a higher coordination number with heterochelate environments, interestingly a variety of compounds with coordination number four, five and six was obtained.

Experimental

All the chemicals used were of AnalaR grade. The reactions were carried out in non-aqueous medium and in inert atmosphere to avoid moisture contamination as far as practicable. The complexes were recrystallised from methanol and the purity was checked by TLC.

Preparation of $[Me_4N][Ni(pyao)Cl_2]$, $[Me_4N][Ni(acac)Cl_2]$, $[Me_4N][Ni(mbt)Cl_2]$, $[n\text{-cepy}][NiCl_3(\gamma\text{-pic})]$, $[n\text{-cepy}][NiCl_3(pyNO)]$ and $[n\text{-cepy}][NiCl_3(4CNpyNO)]$

An ethanolic solution of tetramethylammonium chloride (0.01 mol) was mixed with an ethanolic solution of uninegative bidentate ligands, viz. pyridyl-2-aldoxime/acetylacetone/2-mercaptobenzothiozole (0.01 mol) in 1:1 molar ratio and stirred well. The resulting mixture was then added to an ethanolic solution of $NiCl_2 \cdot 6H_2O$ (0.01 mol) followed by dropwise addition of dilute ammonium hydroxide solution when the complexes (yield 75%) separated out. The complex was then suction filtered, washed with ethanol, followed by ether and dried *in vacuo*.

A similar method was adopted for the preparation of n-cetylpyridinium complexes with neutral monodentate ligands like γ-picoline, pyridine-*N*-oxide and 4-cyanopyridine-*N*-oxide.

---

*Present address: North Eastern Regional Institute of Science & Technology, Itanagar.

**Author to whom correspondence should be addressed.

0020-1693/91/$3.50

© Elsevier Sequoia/Printed in Switzerland

TABLE 1. Analytical data of the complexes

No.	Complex (Colour)	Molecular weight: found (calc.)	Melting point °C	Found (calc.) (%)					Δ_m (mhos)	μ_{eff} (BM)
				Ni	Cl	S	C	H		
1	$[Me_4N][Ni(pyao)Cl_2]$	328.01	>250	17.7	21.20		37.00	5.95	142.0	3.3
	(Buff)	(324.81)		(18.0)	(21.85)		(36.94)	(5.23)		
2	$[Me_4N][Ni(acac)Cl_2]$	310.51	222	19.81	25.32		35.82	7.31	121.5	2.9
	(Sky Blue)	(302.93)		(19.38)	(23.43)		(35.65)	(6.27)		
3	$[Me_4N][Ni(mbt)Cl_2]$	373.80	>250	16.12	19.2	18.15	35.81	4.31	132.4	3.0
	(Brown)	(370.07)		(15.86)	(19.18)	(17.33)	(35.66)	(4.32)		
4	$[n\text{-}cepy][NiCl_3(\gamma\text{-}pic)]$	565.33	>250	10.31	20.13		57.60	7.62	101.6	3.2
	(Light Blue)	(562.85)		(10.43)	(18.92)		(57.56)	(7.81)		
5	$[n\text{-}cepy][NiCl_3(pyNO)]$	571.25	>250	10.15	18.7		55.00	7.88	148.0	3.6
	(Yellow)	(564.82)		(10.39)	(18.85)		(55.23)	(7.43)		
6	$[n\text{-}cepy][NiCl_3(4CNpyNO)]$	589.92	>250	9.90	18.12		52.7	7.10	126.4	3.4
	(Yellow)	(589.72)		(9.95)	(18.06)		(52.90)	(7.12)		
7	$[Me_4N][Ni(et_2dtc)_2Cl]$	469.30	>250	13.02	7.65	27.1	36.91	6.91	126.3	3.01
	(Bottle Green)	(465.36)		(12.6)	(7.6)	(27.50)	(36.10)	(6.8)		
8	$[Me_4N][Ni(OX)_3]$	572.11	>250	10.30			65.25	5.12	105	3.0
	(Light Yellow)	(565.79)		(10.30)			(65.74)	(5.30)		

Preparation of $[Me_4N][Ni(et_2dtc)_2Cl]$

An ethanolic solution of tetramethylammonium chloride (0.01 mol) was mixed with excess of an ethanolic solution of the sodium salt of diethyldithiocarbamate (0.03 mol) and stirred well. The resulting solution was added to an ethanolic solution of $NiCl_2 \cdot 6H_2O$ (0.01 mol) with stirring, followed by the dropwise addition of dilute ammonia solution till a dark green solid product (yield 75%) separated out. It was then suction filtered, washed with ethanol, ether and dried *in vacuo* over anhydrous calcium chloride.

Preparation of $[Me_4N][Ni(OX)_3]$

An ethanolic solution of tetramethylammonium chloride (0.01 mol) was mixed with excess of an ethanolic solution of 8-hydroxyquinoline (oxine) (0.03 mol) and the resulting solution was added to $NiCl_2 \cdot 6H_2O$ in ethanol medium with stirring. The resulting solution was neutralised with ammonia solution when yellowish green solid products (yield 75%) were separated out. These were suction filtered, washed with ethanol, ether and dried *in vacuo*.

Physical measurements

Nickel, sulfur and chloride were estimated by standard methods [14]. Carbon and hydrogen analyses were performed by a System Control semiautomatic instrument. The conductance measurements of $\sim 10^{-3}$ M solution in methanol medium were carried out using a Systronics-303 direct reading conductivity meter with a dip type cell. The magnetic susceptibility measurements were carried out for solid specimens at room temperature (25 ± 1 °C) with a Gouy balance using $Hg[Co(NCS)_4]$ as calibrant. Diamagnetic corrections were calculated using Pascal's constants [15]. The infrared spectra of the compounds were recorded in the region 4000–200 cm^{-1} using a Perkin-Elmer 1420 ratio recording spectrophotometer as KBr pellets. The electronic spectra of the solution in methanol medium were obtained using an Elico-CL-54D spectrophotometer. The molecular weight determination was carried out by Rast's method using biphenyl as solvent. The analytical data are given in Table 1 and infrared and electronic spectral data are presented in Table 2.

Results and discussion

All the compounds have elemental analyses consistent with their formulations. The molar conductance values of 101.6–148.2 mhos in methanol medium indicate that the compounds are 1:1 electrolytes [16] (Table 1). For Ni^{2+} in tetrahedral symmetry and $\lambda = -315$ cm^{-1}, the magnetic moment at room temperature should lie between 3.6 and 4.0 BM and should fall markedly with temperature. If the ligand field departs from tetrahedral symmetry or electron delocalisation occurs, the moment tends to be closer to the spin-only value (2.38 BM) and vary to a lesser extent with temperature. The magnetic moment values of the four-coordinate complexes (nos. **1**–**6**, Table 1) found in the range 2.9–3.6 BM indicated the

TABLE 2. Infrared and electronic spectral data of Ni(II) complexes

No.	Complex	Infrared spectra (cm^{-1})				Electronic spectra (cm^{-1})	
						$^3T_1(F) \rightarrow {}^3T_1(P)$ (ν_3)	$^3T_1(F) \rightarrow {}^3A_2(F)$ (ν_2)
		Me_4N	pyao	νN–O			
1	$[Me_4N][Ni(pyao)Cl_2]$	775, 930	1040			15873	11904
			acac				
			νC=C	νC=O			
2	$[Me_4N][Ni(acac)Cl_2]$	765, 930	1620	1520		15873	12195
			mbt				
			ν_sN–C=S	ν_{as}N–C=S			
3	$[Me_4N][Ni(mbt)Cl_2]$	750, 930	1440	1330		16666	12195
		n-cepy	γ-pic				
			νC=C + νC=N				
4	$[n\text{-cepy}][NiCl_3(\gamma\text{-pic})]$	3050	1610	1550		16666	11764
			pyNO				
			νN–O	δN–O	γC–H		
5	$[n\text{-cepy}][NiCl_3(pyNO)]$	3050	1255	850	740	15873	11764
6	$[n\text{-cepy}][NiCl_3(4CNpyNO)]$	3050	1250	850	740	16666	11904
		Me_4N	et_2dtc				
			νC–S	νC–N			
7	$[Me_4][Ni(et_2dtc)_2Cl]$	775, 980	985	1500		[a]	
			OXνC=O				
8	$[Me_4N][Ni(OX)_3]$	750, 950	1095			[a]	

[a] Electronic spectral data of these complexes are given in the text.

presence of two unpaired electrons. This is expected for a spin free Ni^{2+} complex with tetrahedral configuration as discussed above. On the magnetic consideration, the five-coordinated complexes fall into two categories: diamagnetic with no unpaired electrons ($S=0$) or paramagnetic with two unpaired electrons ($S=1$). The μ_{eff} value of 3.01 BM exhibited by the pentacoordinated complex, $[Me_4N][Ni(et_2dtc)_2Cl]$ at room temperature suggests the presence of paramagnetic species in the complex. The μ_{eff} value for the six-coordinated complex was found to be 3.0 BM at room temperature. The value is consistent with that of a high spin octahedral complex for divalent nickel.

Infrared spectra

The relevant infrared absorption bands due to the coordinated chelates of the complexes with their possible assignments are given in Table 2. Bands due to the tetramethylammonium ion were obtained at 700–800 and 920–980 cm^{-1}. A sharp band was observed at 3050 cm^{-1} due to N–H stretching frequency of the n-cetylpyridinium ion. The ligand acetylacetone can coordinate with a variety of coordination modes [7, 17–20]. In the acetylacetonato chelates of nickel, the νC=O band was found at 1620 cm^{-1} and the νC=C band at 1520 cm^{-1} (Table 2) indicating that the ligand was coordinated to the metal ion as a uninegative bidentate one through the oxygen atoms. Similar observations were also reported by Graddon [21]. In 2-mercaptobenzothiozole the bands νN–C=S, νC–N and δN–H bands were found to be absent, which indicates the deprotonation of the ligand on complexation. The deprotonation was further confirmed by the absence of the N–H stretching band at ~3100 cm^{-1}. Thus the ligand behaves as a uninegative bidentate one in the complex [22–24]. The ligand pyridyl-2-aldoxime was also found to behave as a uninegative bidentate chelate. The νN–O band of the ligand at 1440 cm^{-1} indicated the coordination of metal ion through the oxime nitrogen [12]. The bonding is compatible with the preferred mode of coordination for oximes [25]. The $\nu C \overset{\cdots}{-} C + \nu C \overset{\cdots}{-} N$ bands due to γ-picoline were found at 1610 and 1550 cm^{-1}. The C–H stretching vibration of the pyridine ring was found to overlap with the bands of the n-cetylpyridinium ion indicating the coordination of the ligand through the nitrogen atom [26–28]. In the *N*-oxide complexes reported here, bands at ~1250, ~850 and ~740 cm^{-1} are assigned to νN–O, δN–O and γC–H, respectively, indicating that the ligand *N*-oxide coordinates to the metal ion through the oxygen atom [29, 30]. The νC–S and νC–N bands of diethyldithiocarbamate were obtained at 985 and ~1500 cm^{-1} as expected for a ligand with uninegative bidentate nature [31]. One of the bands due to the tetramethylammonium ion was found at 775 cm^{-1} and the other band was found to overlap with the νC–S band of diethyldithiocarbamate. The νC=O band due to oxime was found at 1095 cm^{-1} indicating the coordination of the ligand through nitrogen and oxygen atoms as a uninegative bidentate one [32].

The electronic spectra are of more diagnostic value for the coordination number and geometry of the compounds. For nickel(II) the ground term is $3T_1(F)$ in tetrahedral (*Td*) symmetry. All the tetracoordinated compounds exhibited bands at 11 764–12 195 and 15 873–16 666 cm^{-1} which may be assigned as $^3T_1 \rightarrow {}^3A_2$ (ν_2) and $^3T_1 \rightarrow {}^3T_1(P)$ (ν_3), respectively, as expected for tetrahedral nickel(II) complexes [33]. Bands were obtained at 8000, 10 000, 13 000 and 16 000 cm^{-1} for the complex $[Ni(et_2dtc)_2Cl]$, which support a pentacoordinated stereochemistry for the complex [34, 35]. For the hexacocoordinate complex $[Me_4N][Ni(OX)_3]$ the electronic spectral bands found at 12 048 (ν_1), 14 492 (ν_2) and 22 988 cm^{-1} (ν_3) due to $^3A_{2g} \rightarrow {}^3T_{2g}(F)$, $^3A_{2g} \rightarrow {}^3A_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$, respectively, are almost in agreement with the octahedral geometry for the complex. In the light of the above discussion it is concluded that the first six compounds [nos. 1–6; Table 1] are tetrahedral (sp^3 hybridisation) whereas the compounds nos. 7 and 8 (Table 1) are square pyramidal and octahedral involving sp^3d and sp^3d^2 hybridisation, respectively.

References

1 G. R. Boston and P. Smith, *J. Am. Chem. Soc., 85* (1963) 1006; G. B. Smith, C. H. Leu and T. R. Griffiths, *J. Am. Chem. Soc., 86* (1964) 4794.
2 H. Sigel, B. E. Fischer and E. Farkas, *Inorg. Chem., 22* (1983) 925.
3 H. Sigel and B. E. Fisher, *J. Am. Chem. Soc., 102* (1980) 2998.
4 S. M. Nelson, *Annu. Rep. Prog. Chem., Sect. A, 71* (1974) 288.
5 D. P. Graddon, *Coord. Chem. Rev., 4* (1969) 1.
6 B. Pradhan and D. V. Ramana Rao, *J. Indian Chem. Soc., 54* (1978) 266.
7 S. Kawaguchi, *Variety in Coordination Modes of Ligands in Metal Complexes,* Springer, Berlin, 1988, pp. 75–106.
8 R. G. Gravey, J. H. Nelson and R. C. Ragsdale, *Coord. Chem. Rev., 3* (1968) 375.
9 N. M. Karayannis, J. W. Minkilwiez, L. L. Pytlewski and M. M. Labes, *Inorg. Chim. Acta, 3* (1969) 129.
10 D. H. Brown, D. Kenyon and D. W. A. Sharp, *J. Chem. Soc. A,* (1969) 1474.
11 T. W. Brill and W. D. Wertz, *Inorg. Chem., 9* (1970) 2692.
12 R. A. Krause, N. B. Colthup and D. H. Busch, *J. Phys. Chem., 65* (1961) 2216.
13 M. Baral, B. K. Kanungo and B. Pradhan, *J. Indian Chem. Soc., 63* (1986) 942, 1018; *Indian J. Chem., 27A* (1988) 66; *Acta Ciencia Indica, 14C* (1988) 303.
14 J. Basselt, R. C. Denney, G. H. Jeffery and J. Mendham, *Vogel's Text Book of Quantitative Inorganic Analysis,* Longman, Harlow, U.K., 1982.
15 P. W. Selwood, *Magnetochemistry,* Interscience, New York, 2nd edn., 1956, pp. 78, 92, 93.
16 W. J. Geary, *Coord. Chem. Rev., 7* (1971) 110.
17 S. Pinchas, B. L. Silver and L. Laulicht, *J. Chem. Phys., 46* (1967) 1506.
18 H. Musso and H. Junge, *Tetrahedron Lett., 33* (1966) 4003, 4009.
19 Y. Nakamura and S. Kawaguchi, *Chem. Commun.,* (1968) 716.
20 J. Lewis, R. F. Long and C. Oldham, *J. Chem. Soc.,* (1965) 6740; D. Gibson, J. Lewis and C. Oldham, *J. Chem. Soc.,* (1966) 1453.
21 D. P. Graddon, *Coord. Chem. Rev., 4* (1969) 1.
22 R. F. Wilson and P. Merchant, *J. Inorg. Nucl. Chem., 29* (1967) 1993.
23 M. C. Flett, *J. Chem. Soc.,* (1953) 347.
24 M. M. Khan and A. U. Malik, *J. Inorg. Nucl. Chem., 34* (1972) 1847.
25 E. Frasson, C. Panattoni and R. Zanetti, *Acta Crystallogr., 12* (1959) 201.
26 Z. A. Siddiqui, M. Shkir, M. Aslam, T. A. Khan and S. A. A. Zaidi, *Synth. React. Inorg. Met-Org. Chem., 13* (1983) 397.
27 R. C. Paul and S. L. Chadha, *Indian J. Chem., 6* (1968) 272.
28 R. C. Paul and S. L. Chadha, *Spectrochim. Acta, 22* (1966) 615.
29 N. M. Karayannis, J. T. Cronin, C. M. Mikulski, L. L. Ptyleski and M. M. Labes, *J. Inorg. Nucl. Chem., 33* (1971) 4344.
30 I. S. Ahuja and R. Singh, *J. Inorg. Nucl. Chem., 35* (1973) 561.
31 R. M. Golding, C. M. Harries, K. J. Jessop and W. Tennat, *Aust. J. Chem., 25* (1922) 2567.
32 R. C. Charles, H. Preisen, R. Friedel, L. E. Hillard and W. D. Johnston, *Spectrochim. Acta, 8* (1956) 1.
33 A. B. P. Lever, *Inorganic Electronic Spectroscopy,* Elsevier, Amsterdam, 1968, pp. 11, 343–344.
34 L. Sacconi, G. P. Speroni and R. Morrasi, *Inorg. Chem., 7* (1968) 1521.
35 I. Bertini and F. Mani, *Inorg. Chem., 9* (1970) 248.