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*Contribution from the Department of Inorganic and Physical Chemistry,
Indian Institute of Science, Bangalore-12, India*

Ambidentate Coordination of the Oxime Group in 1-ethoxycarbonyl-2-alkylimino-1-propanone oximato)(1-ethoxy-(carbonyl-2-imino-1-propanone oximato)nickel(II) Complexes

R.R. Iyengar, K.S. Bose, and C.C. Patel

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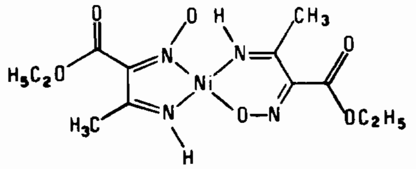
Mixed ligand complexes, of the formula (1-ethoxycarbonyl-2-alkylimino-1-propanone oximato)(1-ethoxycarbonyl-2-imino-1-propanone oximato)Ni^{II}, Ni(R-IEI)(IEI′), where R = CH_3, C_2H_5, n-C_3H_7 n-C_4H_9 or C_2H_4-OH, have been prepared. The electrical conductance in acetone shows the non-electrolytic nature of the complexes while the cryoscopic molecular weight determination in benzene indicates their monomeric nature. The diamagnetic character shows square-planar stereochemistry for these complexes. The ir and nmr spectra suggest the coordination of the isonitroso group of R-IEI through nitrogen and that of IEI′ through the oxygen.

Introduction

Recently, there has been a renewed interest in the coordination behaviour of ligands containing both isonitroso (oxime) and imine functions.[1-6] It has been suggested that in bis(isonitrosoacetylacetoneimino)-Ni^{II}[1,2] and (N-alkylisonitrosoacetylacetoneimino)(isonitrosoacetylacetoneimino)Ni^{II},[2] one of the ligands coordinates through the nitrogen and the other through the oxygen of the isonitroso group. X-ray sructural analysis has confirmed this mode of coordination in the case of (N-methylisonitrosoacetylacetoneimino)(isonitrosoacetylacetoneimino)Ni^{II}.[7] The factors determining such ambidentate coordination are, however, not clear. Because of the close similarity in the structure of isonitrosoethylacetoacetateimine(HIEI, 1-ethxoycarbonyl-2-imino-1-propanone oxime) and isonitrosoacetylacetoneimine(HIAI, 4-imino-2,3-pentanedione 3-oxime) it is of interest to know the coordination behaviour of the former.

Lacey *et al.*[1] have recently suggested that bis(1-ethoxycarbonyl-2-imino-1-propanone oximato)Ni^{II}, Ni(IEI)(IEI′), has a structure (I) similar to that of the corresponding isonitrosoacetylacetoneimine complex. The present investigation has been carried out to have a more detailed understanding of the coordination behaviour of HIEI towards nickel(II).



I

Ni(IEI)(IEI′)

Here IEI and IEI′ represent ligands with N and O coordinated isonitroso groups respectively.

Experimental Section

Materials Used. Nickel acetate tetrahydrate was prepared by dissolving nickel hydroxide in glacial acetic acid and allowing it to crystallise by slow evaporation at room temperature. Isonitrosoethylacetoacetate was prepared from ethylacetoacetate (Riedel) by the method of Wolff *et al.*[8] Ni(IEI)(IEI′) has been prepared by the method of Ewbank and Taylor.[6]

Methylamine (Riedel, 33% aqueous solution), ethylamine (Riedel, 50% aqueous solution), n-propylamine

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(1) M.J. Lacey, C.G. MacDonald, J.S. Shannon, and P.J. Collin, *Aust. J. Chem.*, *23*, 2279 (1970).

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(6) T.W.J. Taylor and E.K. Ewbank, *J. Chem. Soc.*, 2818 (1926).

(7) M.J. Lacey, C.G. MacDonald, J.F. McConnell, and J.S. Shannon, *Chem. Comm.*, 1206 (1971).

(8) L. Wolff, P. Bock, G. Lorentz, and P. Trappe, *Ann.*, *325*, 134 (1902).

(Fluka) and n-butylamine (Riedel) and monoethanolamine (E. Merck) were used as such. Concentrated aqueous ammonia used had a density of 0.88 g/ml. Acetone, benzene and chloroform (A.R., B.D.H.) were used without further purification.

Methods and Apparatus. The conductivity of the complexes in acetone was measured using a Siemen's conductivity bridge. The molecular weight of the complexes in benzene was determined by the cryoscopic method. The magnetic susceptibility was determined by the Gouy technique using $Hg[Co(NCS)_4]$ as the calibrant. Infrared spectra of the complexes in Nujol mull and in chloroform were recorded on a Carl-Zeiss UR-10 spectrophotometer fitted with LiF, NaCl and KBr prisms while the electronic spectra of the complexes in the region 40,000-10,000 cm^{-1} in chloroform were recorded on a Unicam recording spectrometer SP 700A. The proton magnetic resonance spectra of the complexes in $CDCl_3$ were recorded at 31.5°C on a Varian HA-100D spectrometer using precalibrated paper and tetramethylsilane as the internal standard.

Preparation of the complexes. (a) (1-ethoxycarbonyl-2-alkylimino-1-propanone oximato)(1-ethoxycarbonyl-2-imino-1-propanone oximato)Ni^{II}, Ni(R-IEI)(IEI′), where R = CH_3, n-C_3H_7, n-C_4H_9 or C_2H_4OH: To a solution of nickel acetate (1 g, ~0.004 mole) in 70 ml of 50% aqueous ethanol containing 1 ml of the required amine (R-NH_2) and 2ml of ammonia, isonitrosoethylacetoacetate (1.28 g, ~0.008 mole) was added. The dark green solution obtained was then heated on a steam bath until most of the alcohol was removed (50-80 min.). This solution with the crystalline precipitate formed was cooled and filtered. The precipitate was washed with 1:2 alcohol-water mixture and dried in vacuum over concentrated H_2SO_4 The complex was crystallised from 1:1 alcohol-water mixture. Yield: R = CH_3, 90%; n-C_3H_7, 78%; n-C_4H_9, 81%; C_2H_4OH, 60%.

This procedure did not succeed for the preparation of the ethyl derivative, as a black oily material was formed on heating.

(b) Ni(Et-IEI)(IEI′); (Et = C_2H_5). The procedure was similar to that in (a) except that after the additio nof isonitrosoethylacetoacetate the whole solution was kept at room temperature for 12 hrs. Then most of the alcohol was removed under suction and the orange yellow precipitate was filtered, washed and crystallised as before. Yield, 74%.

This procedure is applicable to the preparation of the other complexes also, and gives good yield, (60-75 per cent).

All the complexes are stable crystalline solids, having good solubility in common organic solvents. The molecular weights of the complexes in benzene together with their melting points and colour are given in Table I.

Analysis. Nickel(II) in the complexes was analysed as nickel dimethylglyoximate after decomposing the complexes with a mixture of sulphuric, nitric and perchloric acids. Carbon, hydrogen and nitrogen were analysed by microanalytical methods at I.I.T., Kanpur, through the kind courtesy of Prof. C.N.R. Rao. The analytical results are given in Table I.

Results and Discussion

The molar conductance of the complexes (<1 ohm^{-1} cm^2 $mole^{-1}$) in acetone shows them to be non-electro-

Table I. Colour, melting point, molecular weight and analytical data of Ni(IEI)(IEI′) and Ni(R-IEI)(IEI′) complexes.

Complexes	Colour	M.P.	Molecular weight		Analytical data Found %				Calcd. %			
		°C	Calcd.	Found	Ni	C	H	N	Ni	C	H	N
Ni(IEI)(IEI′)	Deep yellow	205	—	—	15.74	38.64	4.86	15.02	15.72	38.99	4.84	15.05
Ni(CH_3-IEI)(IEI′)	Orange	152	387	372	15.17	40.33	5.21	14.47	15.25	40.23	5.00	14.25
Ni(C_2H_5-IEI)(IEI′)	Yellow orange	144	401	397	14.64	41.93	5.53	13.97	14.99	41.60	5.85	13.80
Ni(n-C_3H_7-IEI)(IEI′)	Orange red	134	415	418	14.15	43.42	5.80	13.50	14.31	43.34	5.75	13.78
Ni(n-C_4H_9-IEI)(IEI′)	Yellow	113	429	420	13.68	44.78	6.11	13.09	13.71	45.12	6.23	13.20
Ni(C_2H_4OH-IEI)(IEI′)	Pale orange	170	417	432	14.08	40.31	5.32	13.44	14.01	40.10	5.42	13.62

Table II. Electronic spectral bands of Ni(IEI)(IEI′) and Ni(R-IEI)(IEI′) complexes in $CHCl_3$. Absorption maxima in cvm^{-1} and ε^a in litre $mole^{-1}$ cm^{-1}.

Ni(IEI)(IEI′)	39,700 (2.37×10^4)	33,100 (1.85×10^4)	29,900 (1.73×10^4)	26,000 (sh)
Ni(CH_3-IEI)(IEI′)	39,700 (1.81×10^4)	33,300 (1.58×10^4)	29,400 (1.35×10^4)	26,700 (sh)
Ni(C_2H_5-IEI)(IEI′)	40,000 (2.25×10^4)	33,300 (1.84×10^4)	29,900 (1.68×10^4)	26,000 (sh)
Ni(n-C_3H_7-IEI)(IEI′)	39,800 (2.21×10^4)	33,400 (1.95×10^4)	29,900 (1.65×10^4)	26,300 (sh)
Ni(n-C_4H_9-IEI)(IEI′)	40,000 (2.26×10^4)	33,100 (1.97×10^4)	30,300 (1.70×10^4)	26,300 (sh)
Ni(C_2H_4OH-IEI)(IEI′)	39,700 (2.31×10^4)	33,300 (2.05×10^4)	29,400 (1.64×10^4)	26,300 (sh)

[a] ε in brackets.

Table III. Important infrared bands of Ni(IEI)(IEI′) and Ni(R-IEI)(IEI′) complexes.

Complexes	C=O stretch in mull cm^{-1}	C=O stretch in $CHCl_3$ cm^{-1}	N-H stretch in mull cm^{-1}	N-H stretch in $CHCl_3$ cm^{-1}	N-O(N-coordinated) stretch in mull cm^{-1}
Ni(IEI)(IEI′)	1700	1700 (sh)	3179	3220	1198
	1720	1715	3310	3375	
Ni(CH_3-IEI)(IEI′)	1698	1700 (sh)			
	1723	1718	3188	3180	1208
Ni(C_2H_5-IEI)(IEI′)	1700	1702 (sh)			
	1715	1718	3180	3200	1205
Ni(n-C_3H_7-IEI)(IEI′)	1699	1700 (sh)			
	1715	1718	3175	3180	1205
Ni(n-C_4H_9-IEI)(IEI′)	1700	1700 (sh)			
	1712	1718	3170	3178	1205
Ni(C_2H_4OH-IEI)(IEI′)	1710	1700 (sh)			
	1720	1720	3175	3180	1202

Table IV. Proton magnetic resonance signals (in τppm) of Ni(IEI)(IEI′) and Ni(R-IEI)(IEI′) complexes with their assignments.

Complexes	$\underline{CH_3}C(=N-)-$ of R-IEI	$\underline{CH_3}C(=N-)-$ of IEI′	$>C=\underline{NH}$ of IEI	$>C=\underline{NH}$ of IEI′	$\underline{CH_3}CH_2-O-$	$CH_3\underline{CH_2}^*-O-$	N-R
Ni(IEI)(IEI′)	7.55^d	7.52^d	2.34	1.16	8.64^t 8.67^t	5.68^{qn} (5.64^q, 5.71^q)	—
Ni(CH_3-IEI)(IEI′)	7.72	7.52	—	1.04	8.62^t 8.65^t	5.66^{qn} (5.62^q, 5.69^q)	6.90
Ni(n-C_3H_7-IEI)(IEI′)	7.72	7.53^d	—	1.01	8.62^t 8.66^t	5.67^{qn} (5.63^q, 5.69^q)	6.59^t 8.30^s 8.99^t
Ni(C_2H_4OH-IEI)(IEI′)	7.63	7.61^d	—	0.81	8.63^t 8.68^t	5.67^{qn} (5.64^q, 5.70^q)	6.05^c 6.45^c

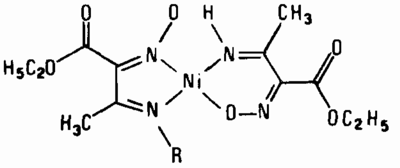
* The two signals given in brackets occur overlapped as a quintet. d, doublet; t, triplet; qn, quintet; q, quartet; s, sextet; c, complex multiplet.

lytes. The monomeric nature of the complexes is shown by their molecular weights in benzene (Table I).

All the complexes are diamagnetic, indicating their square-planar stereochemistry. The electronic spectra of all the complexes including Ni(IEI)(IEI′) in chloroform are given in Table II. The band position of Ni(R-IEI)(IEI′) are closely similar to those of Ni-(IEI)(IEI′) indicating their close structural similarity. The shoulder around 26,000 cm^{-1} is probably due to the expected d-d transition for square-planar nickel(II) complexes.

The ir spectra of Ni(R-IEI)(IEI′) in the solid state and in chloroform are also closely similar to those of Ni(IEI)(IEI′) (Table III). The bands occurring around 1715 and 1700 cm^{-1} in the mull spectra can be assigned to the non-coordinated carbonyl groups of the ester substituent in Ni(R-IEI)(IEI′). In chloroform solution all the complexes including Ni(IEI)(IEI′), however, show one broad band around 1718 cm^{-1} with a shoulder at 1700 cm^{-1}. Although Ni(IEI)(IEI′) in mull shows two N-H stretching frequencies at 3310 (vs) and 3179 (m,b) cm^{-1}, Ni(R-IEI)(IEI′) shows only one band in the region 3170-3188 (m,b) cm^{-1}. The disappearance of the 3310 (vs) cm^{-1} band can be attributed to the replacement of one of the N-H hydrogens of Ni(IEI)(IEI′) by an alkyl group.

In agreement with the above observations. the pmr spectra show only one N-H proton signal around τ 1 for Ni(R-IEI)(IEI′). On the other hand Ni(IEI)(IEI′) gives two N-H proton signals at τ 1.16 and 2.34 (Table IV) which agree well with those reported by Lacey *et al.*[1] Two methyl resonances around τ 7.53 and 7.72 due to the methyl groups of $CH_3.C(=N-)-$are present in the spectra of Ni(R-IEI)(IEI′), the former is a doublet and the latter a singlet. In Ni(IEI)(IEI′) the corresponding bands occur at τ 7.55 and 7.52 respectively, both being doublets.



II

R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9 or C_2H_4OH

Structure (II) for Ni(R-IEI)(IEI′), similar to that of Ni(IEI)(IEI′)[1] is in agreement with these observations. This structure is closely similar to the structure proposed for (N-alkylisonitrosoacetylacetoneimino)(isonitrosoacetylacetoneimino)Ni^{II}.[2,7]

Assignments of some of the ir and pmr bands. The ir band of Ni(R-IEI)(IEI′) and Ni(IEI)(IEI′) occurring around 3180 cm^{-1} can be assigned to the N-H stretch of IEI′ and the band of the latter complex at 3310 cm^{-1} to the N-H stretch of IEI. The band around 1200 cm^{-1} which is probably coupled,[1] can be assigned to the N-O stretch of the N-coordinated isonitroso group in all the complexes.

The pmr signal of Ni(R-IEI)(IEI′) and Ni(IEI)(IEI′) occurring around τ 1 can be assigned to the N-H proton of IEI′ and that at τ 2.34 of the latter to the N-H proton of IEI. The methyl proton resonances of the $CH_3C(=N-)$-groups of Ni(R-IEI)(IEI′) around τ 7.72 and 7.52 can be assigned to that of R-IEI and IEI′ respectively. The corresponding bands of Ni(IEI)(IEI′) occur at τ 7.55 and 7.52 respectively. The $-CH_2-$ proton resonances of the ester groups occur as a quintet around τ 5.67 in all the spectra due to the overlap of the two expected quartets.

Although the factors determining the ambidentate coordination of isonitroso-imine ligands are not yet clear, the electron withdrawing or donating ability of the substituent on the $>C=NO^-$ carbon appears to be important. The acetyl group in isonitrosoacetylacetoneimine and the ester group in HIEI are electron withdrawing and have closely similar Hammet σ values[9] (0.502 and 0.450 respectively). In contrast, methyl substituent in bis(3-imino-2-butanone oximato)-Ni^{II}, where both the ligands are suggested to coordinate through the isonitroso nitrogen atoms,[4] the substituent on the carbon is an electron donating methyl group (Hammett σ value being –0.170).

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