Department of Inorganic and Physical Chemistry,
Indian Institute of Science, Bangalore 560012, India

Ambidentate Coordination of Isonitroso Group in Mixed Ligand Complexes: Preparation and Structure of (N-Alkylisonitrosoethylmethylketimino) (isonitrosoacetylacetoneimino)Ni^{II}

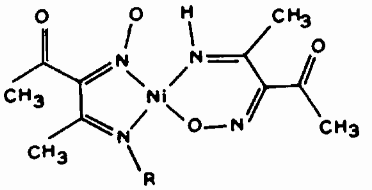
K.S. Bose

Received January 8, 1973

The preparation of (N-alkylisonitrosoethylmethylketimino)(isonitrosoacetylacetoneimino)Ni^{II}, where the alkyl group is methyl, ethyl on n-propyl, is reported. The molecular weight, magnetic susceptibility and infrared, electronic and pmr spectra of these complexes have been studied. It is suggested that N-alkylisonitrosoethylmethylketimine coordinates to nickel(II) through the isonitroso and imine nitrogens, while isonitrosoacetylacetoneimine coordinates through the isonitroso oxygen and imine nitrogen.

Introduction

Recently it has been suggested[1,2] that bis(isonitrosoacetylacetoneimino)Ni^{II} and (N-alkylisonitrosoacetylacetoneimino) (isonitrosoacetylacetoneimino)Ni^{II} have structure I with isonitroso group coordinating through the oxygen or nitrogen. The structure in the case of the N-methyl derivative has been confirmed by X-ray diffraction method[3]. Structure of the type I has also been suggested for the corresponding palladium(II) complexes where R = H^2 or a bulky alkyl group[4]. Nickel(II) complexes of isonitrosoacetoacetic ester imine aer also suggested to have a similar mode of coordination[5]. But in bis(isonitrosoethvlmethylketimino)Ni^{II}, $Ni(IMI)_2$, both the ligands are suggested to coordinate through the isonitroso nitrogen[6,7]. The factors determining the ambidentate coordination of such ligands remain still not clear. This problem is presently being investigated in this laboratory. This report deals with the preparation and characterisation of mixed ligand complexes of nickel(II) containing both isonitrosoacetylacetoneimine(HIAI,4-imino-2,3-pentanedione oxime) and isonitrosoethylmethylketimine(HIMI,3-imino-2-butanone oxime).



I

Ni(R-IAI)(IAI') R= an alkyl group
Ni(IAI)(IAI'), R = H

Experimental Section

Materials used: Isonitrosoacetylacetone was prepared by the method of Wolff et al.[8] and isonitrosoethylmethylketone by the method of Semon and Damerell[9]. Bis(isonitrosoacetylacetoneimino)Ni^{II} was prepared by the procedure of Taylor and Ewbank[10] and crystallised from a 1:1 mixture of ethanol and chloroform. Bis(isonitrosoethylmethylketimino)Ni^{II} was prepared by the method of Pfeiffer[11]. Methylamine (33%), ethylamine (50%) and n-propylamine were Riedel samples. Chloroform (A.R. BDH) was used withouth further purification.

Methods and apparatus: The magnetic susceptibility of the complexes was determined at room temperature by the Gouy method using $Hg[Co(NCS)_4]$ as a calibrant. Molecular weight was determined by the freezing point method using benzene as the solvent. Infrared spectra of the complexes in Nujol mull and chloroform solution were recorded on a Carl-Zeiss UR-10 spectrophotometer fitted with LiF, NaCl and KBr prisms. The electronic spectra of the complexes in chloroform solution were recorded on a Unicam recording spectrophotometer SP 700 A. The proton magnetic resonance spectra of the complexes in $CDCl_3$ were recorded on a Varian HA-100 spectrometer using precalibrated paper and tetramethylsilane as the internal standard.

Preparation of the complexes: (1) (N-Methylisonitrosoethylmethylketimino) (isonitrosoacetylacetoneimi-

---

(1) M.J. Lacey, C.G. MacDonald, J.S. Shannon, and P.J. Collin, *Aust. J. Chem.*, *23*, 2279 (1970).
(2) K.S. Bose, B.C. Sharma, and C.C. Patel, *Inorg. Chem.*, *12*, 120 (1973).
(3) M.J. Lacey, C.G. McDonald, J.F. McConnel, and J.S. Shannon, *Chem. Comm.*, 1206 (1971).
(4) B.C. Sharma, K.S. Bose, and C.C. Patel, *J. Inorg. Nucl. Chem. Letters*, *8*, 805 (1972).
(5) R.R. Iyengar, K.S. Bose, and C.C. Patel, *Inorg. Chim. Acta* *7*, 3 (1973).
(6) A.V. Ablov and V.N. Zubarev, *Russ. J. Inorg. Chem.*, *13*, 1563 (1968).
(7) K.S. Bose, Ph.D. Thesis, *Indian Institute of Science*, Bangalore, 1970.
(8) L. Wolff, P. Bock, G. Lorentz, and P. Trappe, *Ann.*, *325*, 134 (1902).
(9) W.L. Semon and V.R. Damerell, *Organic Syntheses*, Coll., Vol. II, page 204, John Wiley and Sons, New York (1950).
(10) T.W.J. Taylor and E.K. Ewbank, *J. Chem. Soc.*, 2818 (1926).
(11) P. Pfeiffer, *Chem. Ber.*, *63*, 1811 (1930).

Table I. Molecular weight and analytical data of Ni(R-IMI)(IAI') complexes.

Complexes	Molecular weight in benzene		C%		H%		N%		Ni%	
	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
Ni(Me-IMI)(IAI')	310	299	40.63	40.18	5.68	5.40	18.68	18.75	19.31	19.63
Ni(Et-IMI)(IAI')	296	313	43.11	43.21	5.78	5.80	18.42	17.90	18.63	18.75
Ni(n-Pr-IMI)(IAI')	318	327	43.62	44.08	6.55	6.17	16.86	17.14	17.59	17.95

Table II. Infrared and electronic band positions of Ni(R-IMI)(IAI') in cm^{-1}

Complexes	C=O stretch in mull	C=O stretch in $CHCl_3$	N-H stretch in mull	N-H stretch in $CHCl_3$	Electronic spectral band positions in $CHCl_3$*		
Ni(Me-IMI)(IAI')	1692	1693	3127	3148	40,700 (1.33×10^4) 30,500 (1.26×10^4)	35,200 (sh) 27,500 (sh)	33,300 (1.72×10^4)
Ni(Et-IMI)(IAI')	1680	1693	3100	3148	40,700 (1.26×10^4) 30,500 (1.21×10^4)	35,200 (sh) 27,000 (sh)	33,200 (1.61×10^4)
Ni(n-Pr-IMI)(IAI')	1693	1692	3130	3150	40,800 (1.44×10^4) 30,400 (1.35×10^4)	35,100 (sh) 27,400 (sh)	33,100 (1.80×10^4)

* ε litre $mole^{-1}$ cm^{-1} in brackets.

no)Ni^{II}, Ni(Me-IMI)(IAI'): Nickel acetate tetrahydrate (0.5 g) and isonitrosoethylmethylketone (0.5 g) were dissolved in 50 ml of water and methylamine (2 ml) and finely powdered bis(isonitrosoacetylacetoneimino)Ni^{II} were added to it. The suspension was then maintained at 65 – 70°C over a steam bath with stirring. After about 45 min. the temperature was raised to 85°C and kept there for 15 min. The yellow suspension obtained was then cooled well, filtered and washed with water. The compound was crystallised from a 1:1 mixture of acetone and water. Yield 48%, M.P.213°C.

(2) Ni(Et–IMI)(IAI'),($Et=C_2H_5$): Nickel acetate tetrahydrate (0.5 g) and isonitrosoethylmethylketone (0.5 g) were dissolved in 70 ml water. Ethylamine (2 ml) and finely powdered bis(isonitrosoacetylacetoneimino)Ni^{II} were added to the aqueous solution. After keeping the suspension over a steam bath at 65 – 70°C for about 45 min., the temperature was raised to 85°C and maintained there for 5 min. The solution was then filtered hot, cooled in ice and stirred vigorously with a mechanical stirrer for about 30 min. The yellow precipitate formed was filtered, washed with water and crystallised from a 1 : 1 mixture of acetone and water. Yield 25%, M.P. 144°C.

(3) Ni(n-Pr-IMI)(IAI'),($n\text{-}Pr=n\text{-}C_3H_7$): The procedure employed was the same as in the case of the ethyl derivative using the same quantities of the reagents and n-propylamine in place of ethylamine. Yield 17%, M.P. 124°C.

Some properties of the complexes. The complexes are yellow in colour and are stable crystalline solids. They have good solubility in common organic solvents.

Analysis: Nickel in the complexes was analysed gravimetrically 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 Regional Research Laboratory, Hyderabad. The analytical results are given in Table I.

Results and Discussion

All the complexes are monomeric in benzene (Table 1) and are diamagnetic indicating that they have a four-coordinated planar structure. The electronic spectral bands of the complexes (Table II) show a shoulder around 27,300 cm^{-1}, probably due to the expected d-d transition.

The i.r. spectra of the complexes in chloroform (Table II) show only one carbonyl band at 1693 cm^{-1} and one NH stretch at 3148 cm^{-1}. This is consistent with the presence of N-alkylisonitrosoethylmethylketimine and isonitrosoacetylacetoneimine in these complexes, as discussed below. The position and band shape of the NH stretch around 3148 (w, b) cm^{-1} correspond to the 3190 (w, b) band of Ni(R-IAI)(IAI') which has been assigned to the O-coordinated* IAI'[2]. The NH stretch of the N-coordinated ligand of Ni(IAI)(IAI') in chloroform[2] occurs at 3365 (s) cm^{-1}. In $Ni(IMI)_2$, where both the ligands are suggested to coordinate through the nitrogen[6,7] the NH stretch occurs as a sharp and intense band at 3290 cm^{-1} in the mull spectrum (due to low solubility the solution spectrum could not be recorded). From the above evidence one may infer the presence of O-coordinated isonitrosoacetylacetoneimine in the present complexes.

The presence of O-coordinated isonitrosoacetylacetoneimine is further indicated by the position of the carbonyl band which occurs around 1693 cm^{-1}. The

---

* O-coordinated and N-coordinated refer to the coordination of the isonitroso group.

Table III. Pmr signals of Ni(R-IMI)(IAI′), in τ ppm, with their assignments.

Complexes	NH (IAI′	NR (R-IMI)	$CH_3C(=NH)$- (IAI′)	$\mathit{CH}_3C(=NH)$- (IAI′)	C-CH_3 (R-IMI)
Ni(Me-IMI)(IAI′)	0.68	6.93 (CH_3)	7.46	7.50 ^{d} J = 1.3 cps	7.86, 8.05
Ni(Et-IMI)(IAI′)	0.65	6.54 ^{q}, 8.76 ^{t} (CH_2) (CH_3)	7.45	7.49 ^{d} J = 1.4 cps	7.84, 8.06

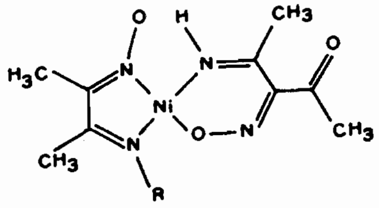
d, doublet; q, quartet; t, triplet.

carbonyl stretching frequencies of Ni(R-IAI)(IAI′) and Ni(IAI)(IAI′) around 1696 and 1672 cm^{-1} in chloroform solution[2] can be assigned to the O-coordinated and N-coordinated ligands respectively. For in $Pd(R\text{-}IAI)_2$, where both the ligands are suggested to be N-coordinated, the carbonyl band occurs near 1673 cm^{-1} in chloroform solution spectra[2]. It may be noted that in Pd(R-IAI)(IAI′) which have a structure similar to Ni(R-IAI)(IAI′) the carbonyl bands occur around 1695 and 1672 cm^{-1} in the mull spectra.

The pmr spectra of these complexes show signals at about τ7.45, 7.50^d, 7.85 and 8.05 which can be assigned to the methyl resonances, excluding those due to the N-alkyl group. The signals at 7.85 and 8.05 can be assigned to the coordinated N-methylisonitrosoethylmethylketimine as the methyl signals of coordinated isonitrosoacetylacetoneimines always occur below τ 7.70[1,2]. The methyl signal of IAI′ at τ 7.50 occurs as a doublet indicating that it is coupled to the NH protons and hence supporting the assignment of the N-methyl substituent to isonitrosoethylmethylketimine. The position of the 7.45 and 7.50^d signals are in closely similar positions to those observed in Ni(IAI)(IAI′) and Ni(R-IAI)(IAI′)[2]. In fact these two signals can be unambigously assigned to an O–coordinated isonitrosoacetylacetoneimine[12]. The NH proton signal of Ni(IAI)(IAI′) due to the O-ccordinated ligand occurs at τ 1.10 and that due to the N–coordinated ligand at τ 2.48. The position of the NH proton signal of Ni(R-IAI)(IAI′) around τ0.66 is near to that of IAI′ in Ni(IAI)(IAI′) and hence further substantiate the O–coordination of IAI′ in the present complexes.

The coordination of R-IMI is expected to be through the isonitroso nitrogen. For it has been observed that the N-alkyl substituted β-isonitroso-imine ligands invariably coordinate through the isonitroso nitrogen[2-6]. Further, in contrast to isonitrosoacetylacetoneimine, both the ligands in bis(isonitrosoethylmethylketimine)Ni^{II} are suggested to coordinate through nitrogen[6,7], which probably indicates that IMI has no tendency to coordinate through oxygen.

On the basis of the above considerations structure II can be assigned to Ni(R-IMI)(IAI′).



II

Although isonitrosoacetylacetoneimine can coordinate through oxygen or nitrogen of the isonitroso group, attempts to prepare complexes containing O–coordinated IMI have not succeeded. As already mentioned, in $Ni(IMI)_2$, both the ligands are suggested to coordinate through the nitrogen of the isonitroso group. This difference in behaviour of these two ligands can be due to the difference in the substituent on$>C=N-O^-$ carbon. In AIA, the substituent is an electron withdrawing acetyl group while in IMI it is an electron donating methyl group. The Hammett σ values are + 0.502 and − 0.170 for the former and the latter respectively[13]. Hence it may be concluded that one of the factors which determines the ambidentate coordination of isonitroso group is the electron withdrawing or donating ability of the substituent on the $>C=N-O^-$ carbon. It is of interest here to mention that in 1-ethoxycarbonyl-2-alkylimino-1-propanone oxime, which can also coordinate through oxygen or the nitrogen of the isonitroso group[1,5], the substituent is an ethoxycarbonyl group which has closely similar electron withdrawing ability as the acetyl group in IAI (Hammett σ value being +0.450[13]).

Acknowledgement: The author thanks Prof. C.C. Patel for his keen interest in this work and encouragements.

---

(12) K.S. Bose, unpublished results.

(13) D.H. MacDaniel and H.C. Brown, *J. Org. Chem.*, 23, 421 (1958).