Asian Journal of Chemistry Vol. 7, No. 2 (1995), 439–441

NOTE

Binuclear Complexes of Nickel(II) with the ligand 1,2,5,6-tetraphenyl-3,4-diaza-1,6-dihydroxyimino-2,4-hexadiene

K. SAHU* and RAJEEV KUMAR SAHU
P.G. Department of Chemistry
B.R.B. College, Samastipur, India

Binuclear complexes of Ni(II) with the ligand 1,2,5,6-tetraphenyl-3,4-diaza-1,6-dihydroxyimino-2,4-hexadiene of the type $Ni_2L_2X_4$ where $X = Cl^-, Br^-, I^-$ or NO_3^- have been isolated. Vibrational spectra suggest co-ordination of the ligand with the metal ions through the azine and oxime nitrogen atoms in a bi-bidentate manner. The complexes are suggested to possess a hydrogen bonded binuclear structure on the basis of IR data. Magnetic data and electronic spectra reveal a tetragonal crystal field around metal ions.

Binuclear complexes of azines and related ligands have evoked great interest in recent years[1–4]. We have reported earlier the inner type binuclear metal complexes of 1,2,5,6-tetraphenyl-3,4-diaza-1,6-dihydroxyimino-2,4-hexadiene with Ni(II), Co(II), Mn(II) and Cu(II).[5] The present paper deals with the isolation of a new series of complexes with Ni(II) where the uncharged ligand acts in a tetrafunctional manner co-ordinating to two metal ions.

α-Benzil monoxime was prepared according to the literature method[6, 7]. The ligand α-benzil azine dioxime was prepared as reported earlier[5] (m.p. 191°C).

Preparation of tetrachloro bis-(1,2,5,6-tetraphenyl-3,4-diaza-1,6-dihydroxyimino-2,4-hexadiene) dinickel(II) $Ni_2L_2Cl_4$

α-Benzil azine dioxime (0.004 mol) was dissolved in minimum quantity of absolute alcohol. Ethanolic solution of $NiCl_2{\cdot}6H_2O$ (0.004 mol) was added to the above solution. The mixture was refluxed for 1 h over a hot water bath. After cooling the solution yellowish crystals separated out. It was filtered, washed with acetone and dried *in vacuo*. Bromo, iodo and nitrato complexes were prepared by similar methods.

The analytical and physical data of the compounds are presented in Table-1. The infrared spectra of the ligand exhibit a band around 3370 cm^{-1} of medium intensity that can be assigned to O—H stretching vibration of N—O—H— group. The —OH stretching vibrations of several oximes involving intramolecular or intermolecular hydrogen bonding are found to occur in 3250–2350 cm^{-1} region[8, 9].

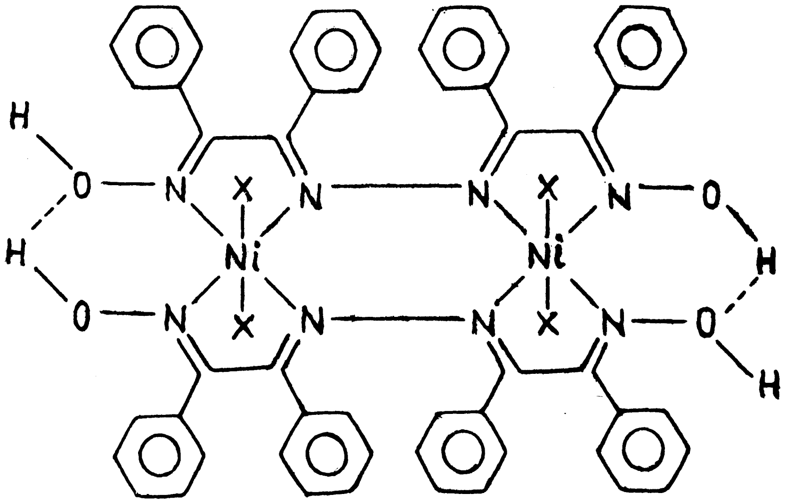
The IR spectrum of the ligand shows multiple bands in the region 3300–2700 cm^{-1} indicating strong inter- or intramolecular hydrogen bonding involving N—O—H— group. In the spectra of the Ni(II) complexes broad bands are observed in this region indicating the existence of hydrogen bonding. A salient feature of the spectra of the ligand is a strong and sharp band at 1645 cm^{-1} which has been assigned to O—H deformation vibration of N—O—H group[10]. Band due to N—O—H deformation persists in the complexes and occurs in the region 1700–1650 cm^{-1} showing the presence of O—H groups and the existence of the ligand in its unionized form. Both the ν(C=N) bands due to the azine and oxime groups shift to higher frequencies in the metal complexes showing co-ordination through nitrogen atoms of these groups. This shift is due to metal to ligand-electron interaction. A band appearing in the region 1090–1050 cm^{-1} in the spectra of the complexes has been assigned to N—O stretching vibration. Besides these bands the spectra show three more bands in the region 1400–1200 cm^{-1} both in the ligand and complexes which can be assigned as phenyl ring vibrations. Thus, on the basis of analytical and IR data the Ni(II) complexes are suggested to have a binuclear hydrogen bonded macrocyclic structure (Fig. 1) with halide ions co-ordinating to complete the tetragonally distorted octahedral structure[11].

TABLE-1
ANALYTICAL DATA OF THE COMPLEXES

Sl. No.	Compounds	% Found (calcd.)				μ_{eff} (B.M.)
		M	C	N	Halogen	
1.	Benzil azine dioxime	—	75.12 (75.33)	12.32 (12.65)	—	—
2.	$Ni_2L_2Cl_4$	9.95 (10.16)	58.05 (58.38)	9.20 (9.73)	12.15 (12.33)	3.10
3.	$Ni_2L_2Br_4$	8.65 (8.80)	50.22 (50.56)	8.22 (8.42)	23.85 (24.07)	3.05
4.	$Ni_2L_2I_4$	7.52 (7.71)	43.95 (44.29)	7.20 (7.38)	33.02 (33.48)	2.80
5.	$Ni_2L_2(NO_3)_4$	9.12 (9.30)	53.12 (53.46)	13.17 (13.36)	—	3.15

L = Benzil azine dioxime

Ni(II) complexes are of high type as the magnetic moment values lie in the region 2.8 to 3.15 per metal ion. Their electronic data are reminiscent of tetragonal field about the metal ion with *trans* —N— atoms and acido groups occupying axial positions. Bands observed near 13,600 cm^{-1} and in the region 14,200 cm^{-1} are assigned to the transitions $^3B_{1g} \rightarrow {}^3B_{2g}$ and $^3B_{1g} \rightarrow {}^3A_{2g}$ respectively. The complexes show a broad band in the region 16,500–18,000 cm^{-1} orginating due to the transition $^3B_{1g} \rightarrow {}^3E_g$ followed by a strong charge transfer band[11, 12].



$X = Cl^-, Br^-, I^-$ or NO_3^-

Fig. 1

REFERENCES

1. W.J. Stratton and P.J. Orgen, *Inorg. Chem.*, **9**, 2588 (1970).
2. J.E. Andrew and A.B. Blake, *J. Chem. Soc.*, 1405 (1969).
3. B.K. Mohapatra and B. Sahoo, *Indian J. Chem.*, **21A**, 376 (1982).
4. S. Satpathy and B. Sahoo, *Curr. Sci. (India)*, **42**, 90 (1973).
5. K. Sahu, *Asian J. Chem.*, **4**, 372 (1992).
6. A.I. Vogel, A Textbook of Practical Organic Chemistry, Longmans, London, p. 720 (1962).
7. E.H. Huntress, Identification of Pure Organic Compounds, John Wiley and Sons, London; Chapman & Hall Limited, p. 610 (1946).
8. R. Blinc and D. Hadzi, *J. Chem. Soc.*, **45**, 36 (1958).
9. A. Palm and H. Werbin, *Can. J. Chem.*, **31**, 1004 (1953).
10. K. Burger, I. Ruff and F. Ruff, *J. Inorg. Nucl. Chem.*, **27**, 179 (1965).
11. C.B. Singh, H.C. Rai and B. Sahoo, *Indian J. Chem.*, **14A**, 504 (1976).
12. A.B.P. Lever, Inorganic Electronic Spectroscopy, 2nd Ed., Elsevier (1984).

(*Received*: 16 March 1994; *Accepted*: 26 September 1994) AJC-881