*Contribution from the Chemical Laboratories,*
*University of Allahabad, Allahabad, India*

# Magnetic and Spectral Studies on a Binuclear Ni (II) - Dimethylaminoethanethiol Complex

**P. C. Jain and H. L. Nigam**

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*Complex formation between Ni(II) and Dimethyl amino ethane thiol-hydrochloride (abbreviated DMAET) has been studied (pH = 7.5 - 8.5). The brown coloured complex thus formed is found to contain two nickel atoms attached through a sulphur bridge, one of them being surrounded octahedrally and the other one remaining in a planar environment as evidenced by magnetic and spectral studies.*

## Introduction

The last decade has witnessed considerable interest in coordination compounds of Ni(II) involving various sulphur donor ligands due to non-availability of relevant data on their donor-acceptor[1-5] relationship. In the present paper dimethyl amino ethane thiol-hydrochloride, $(CH_3)_2N . CH_2 . CH_2 . SH . HCl$ (abbreviation DMAET) a pharmaceutically[6,7] useful and colourimetric reagent for palladium[8] has been found to form a binuclear brown coloured complex with Ni(II) which involves two nickel atoms arranged in octahedral and planar environments respectively.

## Experimental Section

10 ml of 0.05*M* solution of nickel sulphate were added to 50 ml equimolar solution of DMAET in aqueous phase. A brown colour appeared on addition of a few drops of NaOH, maximum intensity of the colour being observed between pH = 7.5 - 8.5. The complex could be extracted with chloroform. After evaporating the solvent, brown residue was washed several times with water. The complex was only slightly soluble in organic solvents. It appeared to dissolve more or less in nitrobenzene. The compound was non-conducting ($\mu$ = 1.4 mhos in $10^{-3}M$) and decomposed at 140°C.

All the materials used were of AnalaR grade. DMAET was Evans Chemetics, N.Y., product of 97.7% purity and its freshly prepared solution was standardised iodometrically.

*Analyses* of the compound showed its formula to be $[Ni_2(DMAET)_4(CHCl_3)_2]$ which required Ni = 15.2%, C = 27.9%, H = 5.4%, N = 7.25% & S = 16.5% and was found to have Ni = 15.09%, C = 28.1%, H = 5.2%, N = 7.2% and S = 16.38%.

*Magnetic measurements* on the above compound were done by Guoy's method at a field strength of 7000 oersted, from 80°K to room temperature (297.9°K). $Hg[Co(CNS)_4]$ was used as calibrating agent ($\chi_g = 16.44 \times 10^{-6}$ c.g.s. at 20°C). The results are given in Table I.

**Table I.**

| Temp. (°K) | $\chi_M \times 10^6$ c.g.s. (uncorrected) | $\chi_{M'} \times 10^6$ c.g.s. (corrected) | $\mu_{eff.}$ (B.M.) | Mean value $\mu_{eff.}$ (B.M.) |
|---|---|---|---|---|
| 80 | 8048 | 8504 | 2.34 | |
| 103 | 5469 | 5925 | 2.22 | |
| 132 | 4286 | 4742 | 2.24 | |
| 168.5 | 3134 | 3590 | 2.20 | 2.26 |
| 200.5 | 2607 | 3063 | 2.22 | |
| 225 | 2337 | 2793 | 2.25 | |
| 297.9 (room temp) | 1678 | 2134 | 2.26 | |

Also the magnetic behaviour of compound was unaltered when the field dependance was checked.

*Absorption Spectra* was recorded on a Carlzeiss spectrophotometer in nitrobenzene using 1 cm quartz cell. Spectral data are given in Table II.

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**Table II.**

| Complex | Medium | Bands ($cm^{-1}$) | Assignment | Stereochemistry |
|---|---|---|---|---|
| $Ni_2(DMAET)_4(CHCl_3)_2$ | $C_6H_5NO_2$ | 17,240 | $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) | Octahedral |
| | | 26,315 | $\rightarrow {}^3T_{1g}$ (P) | |
| | | 22,883 | $^1A_{1g} \rightarrow {}^1A_{2g}$ | Square planar |
| | | 18,510 | $^1A_1 \rightarrow {}^1B_1$ | |

## Discussion

Ni(II) has electron configuration $3d^8$ and is expected to give magnetic moment values of two unpaired electrons in its octahedral[9] and tetrahedral[10] complexes whereas its square planar[11] complexes are expected to be diamagnetic. The magnetic moment value (2.26 B.M.) observed in the present case is much less than the values expected for spin-free octahedral and tetrahedral complexes. This reduction in magnetic moment may be explained on the basis of absorption spectra, which shows four bands appearing at 17240 $cm^{-1}$, 18510 $cm^{-1}$, 22883 $cm^{-1}$ and 26315 $cm^{-1}$ for which the assignments are given in Table II. On taking 10Dq value for the octahedral species to be equal to 9200 $cm^{-1}$ and using Ballhausen's equation,[12] the remaining spin allowed bands are expected to appear at 16560 $cm^{-1}$ and 26240 $cm^{-1}$ which are very close to the observed bands. These are due to the transitions $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) (17240 $cm^{-1}$) and $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) (26315 $cm^{-1}$). The remaining two bands are the characteristic bands of square planar units and correspond to transitions, $^1A_1 \rightarrow {}^1B_1$ (18510 $cm^{-1}$), $^1A_{1g} \rightarrow {}^1A_{2g}$ (22883 $cm^{-1}$). The presence of both octahedral and square planar units accounts for the reduction of magnetic moment. The ligand field stabilization energy for the octahedral unit comes out to be 31.5 kcal/mole.

Thus the complex is found to contain two nickel atoms attached together through a sulphur bridge, one of the nickel atoms being surrounded octahedrally and the other one remaining in a planar environment.

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