

Square-planar adducts of Cu(II) and Ni(II) complexes of some 2-hydroxy acetophenonethiosemicarbazones with nitrogen donors

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Abstract. Square planar nonionic adducts of Cu(II) and Ni(II) of the type ML (base) have been synthesized and characterized. In all these compounds L behaves as dibasic tridentate (ONS) ligand. Ni(II) compounds are diamagnetic while those of Cu(II) show magnetic moment corresponding to one unpaired electron.

Keywords. Square-planar adducts; Ni(II) adducts; Cu(II) adducts; nitrogen bases.

1. Introduction

In continuation of our earlier studies on the coordination of nitrogen bases with nickel(II) complexes (Patil and Shah 1980), we now report the synthesis and characterization of Cu(II) and Ni(II) adducts of the type ML (base), where L is the thiosemicarbazone of a 2-hydroxyacetophenone and base is a monodentate nitrogen or oxygen donor.

2. Experimental

HAT (M.P. 194°C), 3-MeHAT (M.P. 215°C), 4-MeHAT (M.P. 188°C) and 5-MeHAT (M.P. 205°C) were prepared from corresponding ketones using standard methods (Vogel 1956). All solvents and other reagents used were guaranteed reagents. The following general procedure was used in the preparation of adducts of Ni(II) and Cu(II) complexes. While preparing the adducts of ammonia and pyridine, the required amount of ligand was dissolved in the base. In the preparation of adducts of *o*-toluidine, *m*-toluidine, *p*-toluidine and aniline, the required amount of ligand and 2 g of base were dissolved in a minimum amount of ethenol. The solution thus obtained was added to aqueous solution of nickel(II) chloride/ethanolic solution of copper(II) chloride in such a way that M(II) : ligand ratio remained 1 : 1. The reaction mixture was then kept on a steam bath for 30 min and cooled to get the product (red brown in case of Ni(II)

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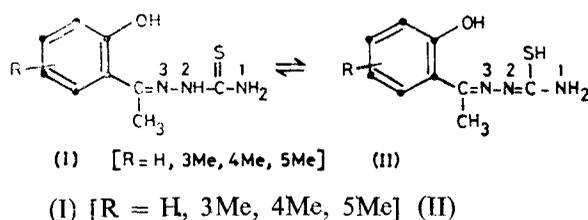
and dark brown in case of Cu(II)). $NiL \cdot H_2O$ were prepared by adding an aqueous solution of sodium acetate to ethanolic 1 : 1 (Ni : L) mixtures. The products thus obtained were filtered and washed with small amounts of ethanol and then with ether and dried by suction.

For establishing the composition, metal content in each adduct was determined by independent gravimetric and volumetric methods. All physico-chemical measurements were made as described earlier (Patil and Shah 1980).

3. Results and discussion

3.1. Nature of the ligands

All the ligands used in the present study may take the following forms :



Some important infrared spectral bands are shown in table 1. Figure 1 shows the infrared spectrum of 3MeHAT. The infrared spectra of the ligands show bands in the ν_{N-H} ($3200-3350\text{ cm}^{-1}$) and ν_{OH} ($3000-3140\text{ cm}^{-1}$) regions. The free ν_{OH} is generally found between $3650-3500\text{ cm}^{-1}$, similar to that of alcoholic ν_{OH} (Califano and Luttko 1955; Brown 1955). The ν_{OH} of several ligands involving

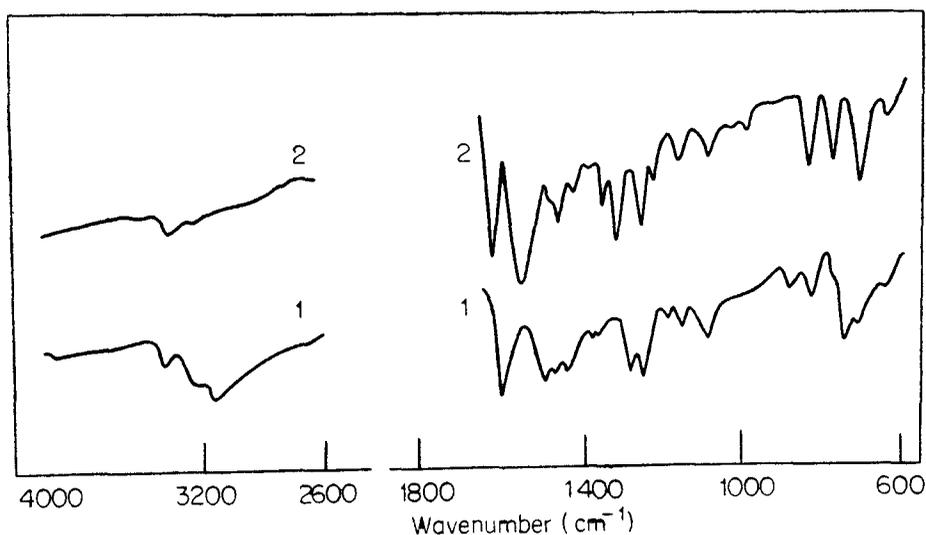


Figure 1. Infrared spectra of 1. 3MeHAT (ligand) and 2. Ni (3MeHAT).

Table 1. Analyses, important infrared spectral and electronic spectral data of adducts of Cu(II) and Ni(II) complexes

| Compound | Metal | Found (calculated) % | | | | Infrared spectral data (in cm ⁻¹) | | | | Electronic spectral data (in cm ⁻¹) |
|--------------------------------|------------------|----------------------|----------------|------------------|---|---|-------------|-------------|-------------------------|---|
| | | C | H | S | | $\nu_{C=N}$ | $\nu_{C=S}$ | ν_{N-N} | | |
| HAT | — | 51.95 (51.69) | 4.99 (5.31) | 15.12 (15.45) | — | 1570s, s | 830s, s | — | — | |
| [Cu (HAT) NH ₃] | 21.84 (22.09) | 34.86 (35.30) | 3.95 (4.24) | 9.86 (10.46) | — | 1560s, m | 740s, s | 970m | 14390 17390 25640 | |
| [Cu (HAT) Py] | 17.85 (18.12) | 47.95 (48.07) | 3.85 (4.29) | 8.78 (9.14) | — | 1550s, s | 750s, s | 950m | 13330 17820 25640 | |
| 3MeHAT | — | 54.48 (54.30) | 5.65 (5.87) | 14.21 (14.52) | — | 1590s, s | 880s, s | — | — | |
| [Cu (3MeHAT) NH ₃] | 20.88 (21.00) | 38.97 (39.74) | 4.32 (4.96) | 10.15 (10.59) | — | 1550s, s | 770s, s | 970m | 14600 17240 25970 | |
| [Cu (3MeHAT) Py] | 17.67 (18.03) | 48.75 (49.39) | 4.27 (4.25) | 8.11 (8.78) | — | 1570s, m | 780s, s | 950m | 13520 17700 25000 | |
| [Ni (3MeHAT) NH ₃] | 19.65 (19.79) | 39.85 (40.66) | 4.87 (5.05) | 10.71 (10.78) | — | 1520s, s | 750s, m | 950m | 17850 24390 | |
| [Ni (3MeHAT) Py] | 16.50 (16.37) | 49.78 (50.20) | 4.35 (4.70) | 8.99 (8.92) | — | 1540s, s | 760 s, s | 970m | 17850 24390 | |
| [Ni (3MeHAT) H ₂ O] | 19.04 (19.14) | 38.86 (39.72) | 5.12 (4.90) | 10.08 (10.46) | — | 1560s, s | 740s, s | 970m | 17770 | |
| [Ni (3MeHAT) <i>o</i> -tolu.] | 15.45 (15.18) | 53.15 (52.76) | 5.44 (5.40) | 8.70 (8.27) | — | 1560s, s | 730s, s | 960m | 24390 18180 24390 | |
| [Ni (3MeHAT) <i>m</i> -tolu.] | 15.58 (15.18) | 51.85 (52.76) | 4.97 (5.40) | 8.80 (8.27) | — | 1560s, m | 740s, s | 980m | 18180 24100 | |

(Contd.)

Table 1. (Contd.)

| Compound | Found (calculated) % | | | Infrared spectral data (in cm^{-1}) | | | Electronic spectral data (in cm^{-1}) | |
|-------------------------------------|----------------------|------------------|----------------|---|--------------------|--------------------|---|-------------------------|
| | Metal | C | H | S | $\nu_{\text{C=N}}$ | $\nu_{\text{C=S}}$ | | $\nu_{\text{N-N}}$ |
| [Ni (3MeHAT) <i>p</i> -tolu.] | 15.35 (15.18) | 53.65 (52.76) | 5.14 (5.40) | 8.83 (8.27) | 1560s, s | 740s, s | 970m | 18020 24100 |
| [Ni (3MeHAT) aniline] | 15.56 (15.75) | 50.85 (51.33) | 3.15 (3.21) | 8.25 (8.58) | 1540s, m | 740s, s | 980m | 17850 24100 |
| 4MeHAT | — | 54.08 (54.30) | 5.62 (5.87) | 14.18 (14.52) | 1580s, m | 860s, s | — | — |
| [Cu (4MeHAT) NH_3] | 20.89 (21.00) | 38.25 (39.74) | 4.15 (4.96) | 10.35 (10.59) | 1550s, s | 750s, s | 970m | 14600 17700 25640 |
| [Cu (4MeHAT) Py] | 17.85 (18.03) | 48.88 (49.39) | 4.35 (4.25) | 8.35 (8.78) | 1550s, m | 770s, s | 980m | 13700 17540 25640 |
| [Ni (4MeHAT) NH_3] | 19.56 (19.79) | 39.98 (40.46) | 4.78 (5.05) | 10.76 (10.78) | 1520s, s | 783s, m | 973m | 18180 24190 |
| [Ni (4MeHAT) Py] | 16.40 (16.37) | 49.54 (50.20) | 4.21 (4.74) | 9.02 (8.92) | 1530s, s | 750s, s | 960m | 17390 24390 |
| [Ni (4MeHAT) H_2O] | 19.14 (18.80) | 38.82 (39.22) | 4.22 (4.90) | 10.62 (10.46) | 1560s, s | 730s, s | 973m | 17970 24390 |
| [Ni (4MeHAT) <i>o</i> -tolu.] | 14.68 (15.18) | 49.96 (50.76) | 4.85 (5.42) | 8.51 (8.28) | 1540s, s | 740s, m | 950m | 17850 24390 |
| [Ni (4MeHAT) <i>m</i> -tolu.] | 14.70 (15.18) | 49.35 (50.76) | 4.87 (5.42) | 8.35 (8.28) | 1540s, m | 770s, m | 970m | 17540 24390 |
| [Ni (4MeHAT) <i>p</i> -tolu.] | 14.65 (15.75) | 50.15 (50.76) | 4.98 (5.42) | 8.49 (8.28) | 1550sh, m | 730s, m | 980m | 18180 24390 |
| [Ni (4MeHAT) aniline] | 15.90 (15.75) | 50.98 (51.33) | 3.10 (3.21) | 8.59 (8.80) | 1540sh, m | 750s, m | 980m | 18180 24390 |

| | | | | | | | | |
|--------------------------------|------------------|------------------|----------------|------------------|-----------|---------|------|-------------------------|
| 5MeHAT | — | 54.52 (54.30) | 5.49 (5.87) | 14.28 (14.52) | 1590s, s | 870s, s | — | — |
| [Cu (5MeHAT) NH ₃] | 21.20 (21.00) | 38.50 (39.74) | 4.10 (4.96) | 10.28 (10.59) | 1560s, m | 760s, m | 970m | 14450 17820 25000 |
| [Cu (5MeHAT) Py] | 17.75 (18.03) | 48.75 (49.39) | 3.95 (4.25) | 8.75 (8.78) | 1550sh, m | 763s, m | 980m | 13520 17700 25000 |
| [Ni (5MeHAT) NH ₃] | 19.67 (19.79) | 41.40 (40.66) | 4.30 (5.05) | 10.43 (10.78) | 1570s, m | 780s, s | 960m | 17850 24390 |
| [Ni (5MeHAT) Py] | 16.16 (16.37) | 50.02 (50.20) | 5.30 (4.70) | 9.23 (8.92) | 1570s, s | 750s, s | 960m | 17850 24390 |
| [Ni (5MeHAT) H ₂ O] | 18.60 (19.14) | 40.20 (39.72) | 4.12 (4.90) | 10.56 (10.46) | 1580s, s | 780s, s | 960m | 17850 24390 |
| [Ni (5MeHAT) <i>o</i> -tolu.] | 15.20 (15.18) | 50.51 (52.76) | 5.30 (5.40) | 8.57 (8.27) | 1560s, m | 820s, m | 960m | 18180 24390 |
| [Ni (5MeHAT) <i>m</i> -tolu.] | 15.06 (15.18) | 51.75 (52.76) | 5.21 (5.40) | 8.79 (8.27) | 1570s, m | 780s, s | 970m | 18180 24390 |
| [Ni (5MeHAT) <i>p</i> -tolu.] | 15.04 (15.18) | 50.65 (52.76) | 5.28 (5.40) | 8.64 (8.27) | 1580s, s | 780s, s | 970m | 18180 24390 |
| [Ni (5MeHAT) aniline] | 16.08 (15.75) | 50.78 (51.33) | 2.95 (3.13) | 8.90 (8.58) | 1550s, s | 780s, m | 960m | 17850 24100 |

s, s = sharp strong; s, m = sharp medium; m = medium, sh, m = shoulder medium.

intramolecular or intermolecular hydrogen bonding is remarkably lower and is dependent on the strength of H-bond formed. The observed low values of ν_{OH} suggest the presence of intermolecular or intramolecular H-bonding in the ligands. An intense strong band at $\sim 860 \text{ cm}^{-1}$ may be assigned to $\nu_{\text{C=S}}$ (Campbell and Grazeskowiak 1967). Absence of any band at $\sim 2570 \text{ cm}^{-1}$ excludes the presence of structure II (Poddar and Saha 1975). The strong band at $\sim 1570 \text{ cm}^{-1}$ may be due to $\nu_{\text{C=N}}$ (Wiles and Suprunchuk 1969). All ligands show two moderately strong bands at ~ 1475 and $\sim 1300 \text{ cm}^{-1}$ which may be due to $\nu_{\text{CN}} + \alpha_{\text{NH}_2} + \nu_{\text{CS}}$ (Mahadevappa *et al* 1976). The band at $\sim 1240 \text{ cm}^{-1}$ may be very safely assigned to $\nu_{\text{CN}} + \nu_{\text{C=S}}$, while the bands at ~ 1160 and $\sim 1000 \text{ cm}^{-1}$ might be due to $\alpha_{\text{NH}_2} + \beta_{\text{NH}_2}$ (Mahadevappa *et al* 1976).

3.2. Nature, bonding and structure of the complexes

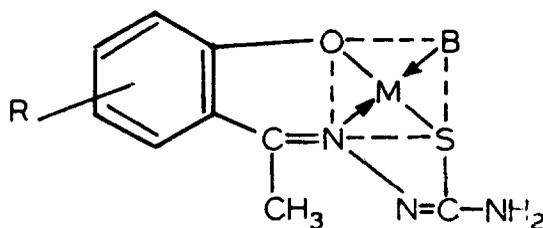
The analytical data (table 1) of the adducts suggest 1 : 1 : 1 (metal : ligand : base) ratio. Their molar conductivities ($2\text{--}17 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) in ethanol indicate their non-ionic nature (Geary 1971).

Some important infrared spectral data are shown in table 1. Figure 1 shows the infrared spectrum of Ni (3MeHAT) Py. The infrared spectra of all the adducts show the absence of ν_{OH} , suggesting the removal of hydroxy proton during coordination. The low energy shifting of $\nu_{\text{C=S}}$ and $\nu_{\text{C=N}}$ in all the adducts, suggest the participation of sulphur and nitrogen³ in coordination (Sujuki 1962; Pradhan and Ramanrao 1971; Sahni *et al* 1977). The ligand band at $\sim 1475 \text{ cm}^{-1}$ shifts to lower energy and the band at $\sim 1300 \text{ cm}^{-1}$ shifts to higher energy on complexation. It may be assumed that the contribution due to $\nu_{\text{C=S}}$ is more in the band at $\sim 1475 \text{ cm}^{-1}$ and the one at $\sim 1300 \text{ cm}^{-1}$ may have more of ν_{CN} . The observed shifting indicates the decrease in bond order of C=S and increase in bond order of C-N. Bands at ~ 1240 , ~ 1160 and $\sim 1000 \text{ cm}^{-1}$ are only slightly affected on complexation (Mahadevappa *et al* 1976). All adducts show a medium band at $\sim 960 \text{ cm}^{-1}$ which may be due to $\nu_{\text{N=N}}$ (Haines and Sun 1968; Cavalca *et al* 1962). This may be due to $\text{N}^2\text{--N}^3$ bond elongation and C=N^2 formation.

Visible reflectance spectrum of each Cu(II) adduct shows broad *d-d* transition with some structures in the range $13000\text{--}18000 \text{ cm}^{-1}$ and a shoulder at 25000 cm^{-1} . The observed bands may be assigned to ${}^2B_{2g} \leftarrow {}^2B_{1g}$ (14000 cm^{-1}) and ${}^2E_g \leftarrow {}^2B_{1g}$ (17000 cm^{-1}) transitions in square-planar stereochemistry (Larkworthy and Patel 1970; Proctor *et al* 1968). The high energy shoulder at 25000 cm^{-1} may be due to charge transfer process. All these adducts show room temperature magnetic moments very close to the spin-only value corresponding to one unpaired electron.

Square-planar complexes of Ni(II) are expected to show bands corresponding to ${}^1A_{2g} \leftarrow {}^1A_{1g}$, ${}^1B_{1g} \leftarrow {}^1A_{1g}$ and ${}^1E_g \leftarrow {}^1A_{1g}$ transitions (Ballhausen 1962; Gray and Ballhausen 1963). All diamagnetic adducts studied here show (table 1) only one band at $\sim 18000 \text{ cm}^{-1}$, which may be assigned to ${}^1A_{2g} \leftarrow {}^1A_{1g}$ transition. The presence of shoulder at $\sim 25,000 \text{ cm}^{-1}$ might be due to charge transfer processes.

The following general structure may be given to the compounds under study



M = Cu(II), Ni(II).

B = NH₃, Py, aniline, *o*-tolu., *m*-tolu., *p*-tolu., H₂O.

R = H, 3-Me, 4-Me, 5-Me.

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