

Studies on some homo and hetero trinuclear complexes of nickel(II), cobalt(II) and copper(II) with 1,8-bis(2'-oxophenyl)-2,3,6,7-tetraza-4,5-dimethyl-1,3,5,7-octatetraene (BTDO)

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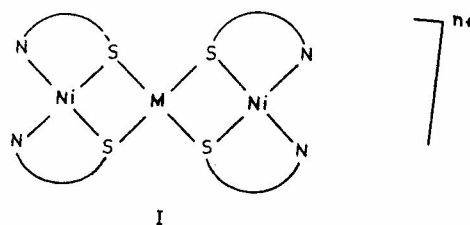
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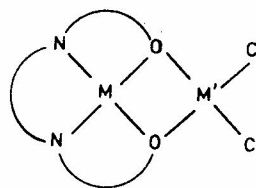
A few homo/hetero trinuclear complexes of the type $[MNiM(BTDO)_2X_2(H_2O)_4]nH_2O$ [where M = nickel(II), cobalt(II) and copper(II), X = Cl^- or NO_3^- , n = 0, or 0.5 and BTDO = 1,8-bis(2'-oxophenyl)-2,3,6,7-tetraza-4,5-dimethyl-1,3,5,7-octatetraene] have been isolated in a stepwise reaction from the precursor nickel bis(diacetyldihydrazone) complexes. These have been characterised on the basis of elemental analyses, spectral and magnetic properties, conductivity measurements and thermal analyses. All the complexes contain coordinated water. The metal centres have an octahedral environmental around them.

The coordinated thio and phenyloxy groups have non-bonding electron pairs which are sufficiently nucleophilic to form bridges with various metal ions¹⁻⁴. As a result, molecules such as bis(2-amino ethylene thio) nickel (II) and N,N'-ethylene bis(salicylidene iminate) metal [M Salen] [M = copper or nickel] can function as bidentate chelating agents (metallo ligands) and form bi- and tri-nuclear complexes of the type (I) (M = Ni, Pd, Cd, Cu or Hg) and (II) (M = Ni or Cu, M' = Cu, Fe or Mn) as shown below.

The metal complexes of dihydrazones of diacetyl, benzil and glyoxal have free amino groups suitably oriented for condensation reaction. Such macrocyclic complexes with these metal complexes have been reported by condensing the complex with formaldehyde^{5,6}. However, no investigation has been made to increase the number of metal centres exploiting these amino groups. In this note we report the preparation and characterization of a few homo/hetero tri-nuclear complexes of these dihydrazone complexes.



I



II

Experimental

All the chemicals used were of BDH or E Merck grade. The solvents were distilled before use. All the other chemicals were used as such. Diacetyldihydrazone and its nickel complexes were prepared following the literature method⁷. Both homo- and hetero- nuclear complexes were prepared by the following two methods.

(i) The ethanolic solutions of bis(diacetyldihydrazone) nickel complex (0.5 mmol) and salicylaldehyde (2 mmol) were refluxed for 2 h and to the resulting solution was added ethanolic solutions of metal salts of copper(II), nickel(II) and cobalt(II) (1mmol) dropwise. After refluxing for 1h again, a clear solution was obtained. It was cooled to room temperature and a calculated amount of NaOH (2. mmol) was added when an intense coloured precipitate was obtained. It was filtered, washed several times with water followed by ethanol and dried over fused $CaCl_2$.

(ii) Hydrazine hydrate (2 mmol) and diacetyl (1mmol) in ethanol were refluxed for 2h and while refluxing the nickel salts (0.5 mmol) in ethanol were added and the refluxing continued for another 1h. It was cooled to room temperature whereupon a precipitate was obtained, which was filtered, washed several times with ethanol and dried over fused $CaCl_2$. The analytical data of this complex corresponds to the nickel bis(biacetyldihydrazone) complex as reported by earlier workers⁷.

Table 1—Analytical data of the complexes

| | Mol. Wt Found (Calc.) | Found (Calc.), % | | | | | | | Λ_M mho cm ² mol ⁻¹ | μ_{eff} (B.M.) |
|--|-----------------------------|------------------|------------------|------------------|------------------|------------------|----------------|----------------|---|------------------------------|
| | | Ni | Cu | Co | N* | C | H | Cl | | |
| Ni ₃ (BTDO) ₂ Cl ₂ 4H ₂ O | 964 (959) | 18.93 (18.35) | — | — | 12.02 (11.67) | 44.81 (45.84) | 4.32 (4.17) | 8.06 (7.40) | 13 | 3.06 |
| Ni ₃ (BTDO) ₂ (NO ₃) ₂ 4H ₂ O | 1021 (1012) | 17.76 (17.39) | — | — | 14.16 (13.83) | 43.34 (42.68) | 3.76 (3.95) | — | 13 | 2.92 |
| NiCu ₂ (BTDO) ₂ Cl ₂ 4.5H ₂ O | 974 (978) | 5.92 (6.00) | 13.42 (13.00) | — | 12.26 (11.45) | 43.42 (44.17) | 4.58 (4.91) | 7.76 (7.25) | 18 | 5.13 |
| NiCu ₂ (BTDO) ₂ (NO ₃) ₂ 4.5H ₂ O* | 1036 (1031) | 5.76 (5.69) | 12.83 (12.33) | — | 13.95 (13.57) | 41.81 (41.90) | 4.17 (3.97) | — | 11 | 4.98 |
| NiCo ₂ (BTDO) ₂ Cl ₂ 4H ₂ O | 963 (960) | 6.35 (6.11) | — | 12.77 (12.29) | 12.05 (11.67) | 45.16 (45.01) | 4.02 (4.16) | 7.71 (7.39) | 16 | 5.39 |
| NiCo ₂ (BTDO) ₂ (NO ₃) ₂ 4H ₂ O | 1023 (1013) | 5.97 (5.79) | — | 12.36 (11.65) | 14.23 (13.82) | 43.05 (42.65) | 3.92 (3.94) | — | 14 | 5.26 |

*Including nitrogen of nitrate group

Since the reaction product of diacetyl and hydrazine hydrate afford the metallo-ligands, we did not isolate it from the reaction products. After refluxing diacetyl and hydrazine hydrate in the presence of nickel salt for 2h salicylaldehyde (4mmol) was added to the reaction mixture and refluxing continued for another 1h. On cooling, a calculated amount of NaOH was added. The precipitate was filtered, washed several times with water followed by ethanol and finally dried over fused CaCl₂. The colour and composition of the complexes thus isolated corresponds to the complexes isolated by method (i). The analytical data of the complexes are presented in Table 1.

The metal and nitrogen content was estimated by the known methods. Carbon and hydrogen were estimated with a MLW-CHN micro analyser. The reflectance and IR spectra of the complexes were recorded on a Cary 2390 and Perkin Elmer 983 spectrophotometer respectively. The conductivities of the complexes in dioxane were measured with a Toshniwal conductivity bridge. The room temperature magnetic moments were determined by Gouy method with Hg[Co(NCS)₄] as calibrant. The molecular weight of the complexes were determined by Rast's method.

Results and discussion

The complexes are coloured and stable at room temperature. They are slowly attacked by dilute acids. They have high melting point (> 250°C) indicating

these to be high molecular weight compounds. All the complexes are soluble in polar solvents such as dioxane, DMF and DMSO.

The metallo schiff base ligand could not be isolated. Hence the spectra of the complexes are compared with the spectra of the parent diacetyldihydrazone⁸ and some known salicylidene complexes⁸. All the complexes exhibit an identical pattern suggesting them to be isostructural.

The IR spectra of the parent nickel diacetyldihydrazone complexes undergo drastic change after schiff base condensation reaction. In the high frequency region, the important characteristic feature of the spectra is the absence of bands in the region 3350-3200 cm⁻¹ and above 1700 cm⁻¹ indicating that condensation has taken place between -NH₂ groups of hydrazone and the carbonyl group of the salicylaldehyde.

A broad band with its centre of gravity at ~ 3450 cm⁻¹ indicates the presence of water molecules. The broadness of the band may be attributed to the presence of strong inter/intramolecular hydrogen bonding. The next pair of bands which are of structural significance are observed as a doublet at ~ 1640 and 1670 cm⁻¹. They can be assigned to $\nu_{\text{C}=\text{N}}$ vibrations. The sharpness, intensity and the splitting of the band is probably due to the presence of two structurally different C=N groups.

Comparing the spectra of the earlier reported diacetyldihydrazone complexes, the band at the

lower frequency region (i.e. $\sim 1640\text{ cm}^{-1}$) is assigned to the azomethine group of the diacetyl fragment while the band $\sim 1670\text{ cm}^{-1}$ correspond to the azomethine group from the salicylidene fragment. The former band in the free ligand (diacetyldihydrazone) was observed⁸ at $\sim 1580\text{ cm}^{-1}$ which shifts to higher frequency region in the complex due to participation of the *d* electron cloud from the metal centre into the ligand orbitals⁷, thereby increasing the degree of conjugation. As a result of this interaction, the bond order of C=N group increases, shifting the C=N to higher frequency region. In the present complexes, they are shifted to still higher frequency region $\sim 1640\text{ cm}^{-1}$ indicating the elongation of conjugated system after condensation has taken place. The splitting of the band to two fragments suggests that the azomethine groups are in different chemical environment.

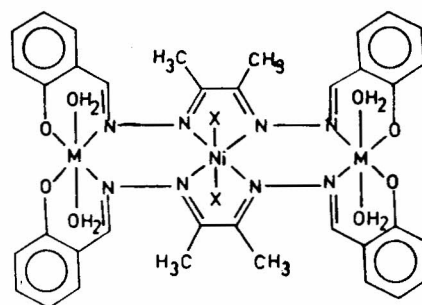
A band $\sim 1480\text{ cm}^{-1}$ attributed to $\nu\text{C-O}$ suggests that deprotonation has taken place at the phenolic OH group of salicylaldehyde⁹. The symmetric and asymmetric $\nu\text{C-CH}_3$ deformation vibration undergo slight shift in their position, the mode of shift being irregular.

All the complexes have low molar conductance values and they also contain anions suggesting them to be coordinated (non-ionic) to the central metal ion. In order to confirm their nature (whether ionic or non-ionic), the spectra of the nitrate complex was recorded. A nitrate group can act as a unidentate or a bidentate ligand. The IR spectra of the nitrate complexes exhibited two additional bands, one in the region $\sim 925\text{-}1050\text{ cm}^{-1}$ (ν_1) and other in the region $\sim 1290\text{-}1200\text{ cm}^{-1}$ (ν_2) which can be attributed to $\nu\text{N-O}$ of NO_3^- group. The third band (ν_3) which is expected to appear for the N-O group in the region $\sim 1530\text{-}1480\text{ cm}^{-1}$ appear to have been overlapped with the deformation vibration of C-CH₃ group. By comparing the spectra with some known unidentate and bidentate complexes¹⁰, we are of the opinion that the nitrate group is coordinated in a unidentate manner in all the nitro complexes.

The lower frequency region ($600\text{-}200\text{ cm}^{-1}$) furnishes information regarding the bonding in the complexes with respect to the ligand moiety. The bands in the region $\sim 530\text{-}510\text{ cm}^{-1}$ and $\sim 460\text{-}440\text{ cm}^{-1}$ are attributed to $\nu\text{M-O}$ and $\nu\text{M-N}$ respectively^{11,12}. Thus from IR spectral data, we conclude that the ligand molecule coordinates to the metal centres through azomethine nitrogens and phenolic oxygen. Comparing the spectral properties of the present series of the complexes with the nickel bis dihydrazone complexes, it seems that the anions are coordinated probably to the central metal ion. The

phenolic OH group undergo deprotonation in the presence of NaOH leaving the ligand as a dianion. Thus the charge on the metal centres are neutralised.

Based on IR data, the following structure for the complexes can be proposed (structure III). It will satisfy the electroneutrality of the complexes as indicated by conductivity measurement.



III

Since IR spectra indicate the presence of water molecules, we undertook thermal studies to ascertain their nature. The decomposition of the complexes follow an identical pattern. There was no weight loss upto 160°C except for copper(II) complexes which lose a mass corresponding to 0.5 molecule of water at $\sim 80^\circ\text{C}$. This is probably due to the presence of lattice water^{13,14}. After 160°C , the complexes lose weight corresponding to four molecules of water in a single step supported by an exothermic peak at the same temperature in the DTA thermogram. Such a behaviour is characteristic of the coordinated water molecules in the same chemical environment. The decomposition proceeds slowly upto $\sim 220^\circ\text{C}$ leaving behind a final residue at 780°C . The residue correspond to the formation of the respective metal oxides.

The reflectance spectra of the complexes are complicated due to the overlapping of bands belonging to different metal ions and their presence in different crystal fields. However, we have made attempts to identify some of these bands. The magnetic moment values have been recorded in Table 1. The spectra of parent⁷ bis(diacetyldihydrazone) nickel(II) complex was compared with the spectra of the present series of complexes. The nickel(II) ion in bis(diacetyldihydrazone) nickel(II) is spin free type and have an octahedral field around it. The spectral characteristics of the complex also suggests an octahedral symmetry with certain degree of tetragonal distortion. It exhibits two bands in the region $14000\text{-}19000\text{ cm}^{-1}$. The lower frequency band corresponds to ${}^3B_{1g} \rightarrow {}^3A_{2g}$ and the higher frequency band assigned to ${}^3B_{1g} \rightarrow {}^3E_g$ transitions respectively.

The ${}^3A_{2g}$ and 3E_g transitions are two splitting components of ${}^3T_{1g}$ state of an octahedral field when subjected to tetragonal distortion. These bands undergo drastic changes when an *in situ* reaction was carried out with the carbonyl compounds.

All the $[\text{Ni}_3(\text{BTDO})_2\text{X}_24\text{H}_2\text{O}]$ complexes exhibit an identical pattern. The parent bands assigned to ${}^3B_{1g} \rightarrow {}^3A_{2g}$ and ${}^3B_{1g} \rightarrow {}^3E_g$ undergo a red shift and is observed in the region 11,300-17,600 cm^{-1} . This suggests that the complexes have been subjected to strong tetragonal distortion. The room temperature magnetic moment value per nickel ion is in the range 2.92-3.06 B.M., which is less than the parent complex.

All the $[\text{NiCu}_2(\text{BTDO})_2\text{X}_24\text{H}_2\text{O}]0.5\text{H}_2\text{O}$ complexes exhibit an identical pattern with the bands due to parent bis(diacetyldihydrazone) nickel(II) complex getting broadened. A broad envelop centered at 15,400 cm^{-1} and 22,200 cm^{-1} were observed. The former band is probably due to parent bis diacetyldihydrazone complex. The latter band can be assigned to ${}^2E_g \rightarrow {}^2T_{2g}$ transition due to copper(II) ion in an approximately octahedral field. The room temperature magnetic moment values lie in the range 4.98-5.13 B.M.

In case of $[\text{NiCo}_2(\text{BTDO})_2\text{X}_24\text{H}_2\text{O}]$ complexes, no well dissolved bands were observed. Hence no assignment could be done. The magnetic moment values lie in the range 4.98-5.13 B.M. Therefore it seems that they are strong field complexes having two paramagnetic cobalt centres.

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