Synthesis & Characterization of Some Mixed Ligand Complexes of Ni(II) Acetylacetonate with Oxygen Donor Ligands

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Received 9 August 1978

A number of alcoholate complexes of nickel(II) acetylacetonate with the general formula Ni(acac)₂·ROH (where R = Me, Et, n-Bu, i-Pr, s-Bu, t-Bu and t-Am) have been synthesized by the reaction of Ni(acac)₃ with excess of alcohol under reflux. These derivatives have been characterized on the basis of the infrared, visible reflectance spectra, magnetic susceptibility, molecular weight measurements and thermogravimetric analysis.

Materials and Methods

Preparative work was carried out under absolute anhydrous conditions. Alcohols were dried by the literature procedures. Nickel was estimated gravimetrically as its dimethylglyoxime complex. Alcohols were estimated by an oxidimetric method after removing them azeotropically with moist benzene.

Visible reflectance spectra of solid complexes in nujol and in chloroform solution were recorded on a Russian C1-10 recording spectrophotometer and near IR spectra, on a Perkin-Elmer 4000A. The IR spectra in the range 4000-200 cm⁻¹ were recorded in KBr on a Perkin-Elmer 621 IR spectrometer. Magnetic susceptibility measurements were made at the room temperature by standard Gony method in benzene solution. Molecular weights were determined in a semi-micro ebulliometer (Gallenkamp) with a thermoster sensing device.

Reaction of Ni(acac)₃ with alcohols — Weighed amounts of anhydrous bis-acetylacetonatonickeI(II), prepared by the method of Charles and Pawlikowski, were treated with excess of dry alcohols. The reaction mixtures were refluxed for 2-3 hr when Ni(acac)₃ dissolved gradually giving a clear green solution. After keeping the solution overnight at the room temperature (ca. 20°), green crystals were obtained which were washed with benzene and finally dried under reduced pressure (1 mm Hg) at temperatures corresponding to boiling points of alcohols. Results are summarized in Table 1.

Results and Discussion

Solvolysis reactions of nickel bis-acetylacetonate in excess of alcohols under strictly anhydrous conditions lead to the formation of complexes of the type Ni(acac)₂·ROH (Eq. 1)

\[ \text{Ni(acac)}_3 + \text{ROH} \leftrightarrow \text{Ni(acac)}_2 \cdot \text{ROH} \]

[where R = Me, Et, n-Bu, i-Pr, s-Bu, t-Bu and t-Am].

These adducts are soluble in parent alcohols as well as in common organic solvents such as acetone, chloroform and dichloromethane.

Nickel acetylacetonate monomethanolate is stable up to 80° (2 mm) and loses 0.5 molecule of methanol at 100-110° (2 mm). At 140° the adduct loses the remaining alcohol. An almost similar pattern of loss of alcohol from the adduct molecule has been found with nickel acetylacetonate monomethanolate.

Infrared spectra (\(\nu_{\text{max}}\) in cm⁻¹) of all the complexes show lowering in the position of the νOH
of alcohols from 3300 (ref. 11) to 3080. This could be explained on the basis of the coordination of the alcohol molecule to the nickel atom. As could be expected on the basis of the observed spectra and perturbation calculations on similar nitrogen donor adducts, νNi–O appearing <700 in nickel acetylacetonate is found to be shifted to lower frequencies in the present oxygen adducts.

Electronic spectra of the compounds have been recorded in chloroform, parent alcohols or in nujol mull and no marked difference could be observed. These spectra are typical of divalent nickel in an octahedral environment with three bands assigned to $^2A_{2g} \rightarrow ^2T_{2g} (F)$, $^2A_{2g} \rightarrow ^2T_{1g} (F)$ and $^2A_{2g} \rightarrow ^2T_{1g} (P)$. The ligand field parameter ($D_q$), the Racah parameter ($B$) and the covalency factor ($\beta$) have been calculated and are summarized in Table 2.

For a $d^8$ system in an octahedral field, the first transition $^2A_{2g} \rightarrow ^2T_{2g} (F)$ represents $10D_q$. The parameter $B$ was obtained by the method of Underhill and Billing. The value of $B$ in all cases was lowered by about 72-82% of the free ion value reflecting the extent of covalent character of the metal-ligand bond.

Magnetic moments of all the derivatives have been measured at the room temperature and the results, reported in Table 2, indicate that all the complexes show a magnetic moments of 3.24 ± 0.06 BM. Six-coordinate octahedral nickel(II) complexes contain two unpaired spins and show magnetic moment about 10-15% above the 'spin-only' value, which may be due to the ferromagnetic interaction in the cluster.

Molecular weights of all the derivatives (Table 1) show that the alcololate complexes of nickel bis-acetylacetonate are dimeric, compared to the trimeric nature of the acetylacetonate itself. The presence of nickel in an octahedral environment is revealed by the magnetic and spectral studies. Nevertheless, more direct experimental evidence would be necessary to reach the final conclusion about their stereochemistry. The plausible structure (I) can be suggested for these adducts.

Acknowledgement

One of the authors (B.P.B.) is grateful to the CSIR, New Delhi, for the award of a senior research fellowship.

References