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

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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 $Ni(acac)_2$ 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.

THE continued interest in the study of nickel(II) bis-acetylacetonate complexes appears to be mainly due to a variety of possible stereochemical configurations[1-3]. Considerable attention has been paid to the addition complexes of Ni(II) acetylacetonate with nitrogen donors, e.g. aliphatic primary amines and pyridine[4-7], but no work appears to have been carried out on the addition complexes with oxygen donors. It was, therefore, considered worthwhile to prepare and characterize the alcoholate complexes of nickel bis-acetylacetonate. Certain interesting changes in the molecular association have been noticed, which are also reported in this paper.

TABLE 1 — ALCOHOLATE COMPLEXES OF NICKEL(II) ACETYLACETONATE

Product	Found (%) (Calc.)		Mol. wt Found (Calc.)
	Nickel	Alcohol	
$Ni(acac)_2.MeOH$	20·21 (20·31)	11·05 (11·10)	549 (289)
$Ni(acac)_2.EtOH$	19·31 (19·37)	15·05 (15·21)	612 (303)
$Ni(acac)_2.Bu^nOH$	17·80 (17·73)	—	651 (331)
$Ni(acac)_2.Pr^iOH$	18·46 (18·52)	18·76 (18·96)	618 (317)
$Ni(acac)_2.Bu^sOH$	17·62 (17·73)	—	678 (331)
$Ni(acac)_2.Bu^tOH$	17·65 (17·73)	—	642 (331)
$Ni(acac)_2.Am^tOH$	16·93 (17·01)	—	704 (345)

Materials and Methods

Preparative work was carried out under absolute anhydrous conditions. Alcohols were dried by the literature procedures[8]. Nickel was estimated gravimetrically as its dimethylglyoxime complex. Alcohols were estimated by an oxidimetric method[9] after removing them azeotropically with moist benzene.

Visible reflectance spectra of solid complexes in nujol and in chloroform solution were recorded on a Russian $C\phi$-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 Gouy method in benzene solution. Molecular weights were determined in a semi-micro ebulliometer (Gallenkamp) with a thermister sensing device.

Reaction of $Ni(acac)_2$ *with alcohols* — Weighed amounts of anhydrous bis-acetylacetonatonickel(II), prepared by the method of Charles and Pawlikowski[10], were treated with excess of dry alcohols. The reaction mixtures were refluxed for 2-3 hr when $Ni(acac)_2$ 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

Solvolytic 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)

$$Ni(acac)_2 + ROH\ (excess) \xrightarrow{reflux} Ni(acac)_2.ROH \quad ...(1)$$

[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 monoethanolate.

Infrared spectra (ν_{max} in cm^{-1}) of all the complexes show lowering in the position of the νOH

TABLE 2 — ELECTRONIC SPECTRA* AND MAGNETIC MOMENTS OF NICKEL (II) ACETYLACETONATE ALCOHOLATES

Compound	$^3A_{2g} \rightarrow {}^3T_{2g}$ (10 Dq)	$^3A_{2g} \rightarrow {}^3T_{1g}$ (F)	$^3A_{1g} \rightarrow {}^3T_{1g}$ (P)	B	β	μ_{eff} (BM)
$Ni(acac)_2$	8800	15267	25210	938	0·87	3·23
$Ni(acac)_2.MeOH$	9175	14810	24415	780	0·72	3·25
$Ni(acac)_2.EtOH$	9210	14900	24666	796	0·74	3·27
$Ni(acac)_2.Bu^nOH$	9240	15070	25365	847	0·78	3·29
$Ni(acac)_2.Pr^iOH$	9302	15110	25770	872	0·81	3·20
$Ni(acac)_2.Bu^sOH$	9260	14910	24472	773	0·72	3·21
$Ni(acac)_2.Bu^tOH$	9346	15315	26092	891	0·82	3·19
$Ni(acac)_2.Am^tOH$	9302	15083	25080	817	0·76	3·18

*Transitions and B in cm^{-1}.

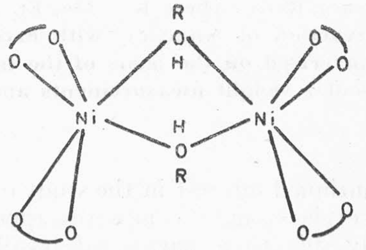
of alcohols from 3300 (ref. 11) to 3080. This could be explained on the basis of the coordination of the alcohol molecule to the nickel atom. As could be expected on the basis of the observed spectra and perturbation calculations on similar nitrogen donor adducts[12], νNi–O appearing <700 in nickel acetylacetonate 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[13] with three bands assigned to $^3A_{2g} \rightarrow {}^3T_{2g}(F)$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$. The ligand field parameter (Dq), the Racah parameter (B) and the covalency factor (β) have been calculated and are summarized in Table 2.

For a d^8-system in an octahedral field, the first transition $^3A_{2g} \rightarrow {}^3T_{2g}(F)$ represents $10Dq$. The parameter B was obtained by the method of Underhill and Billing[14]. 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 $3·24 \pm 0·06$ 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[15].

Molecular weights of all the derivatives (Table 1) show that the alcoholate complexes of nickel bis-acetylacetonate are dimeric, compared to the trimeric nature of the acetylacetonate[1] 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.



(I)

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