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Synthesis and Physico-Chemical Studies of Some Polynuclear Mixed Carboxylate Complexes of Nickel(II)

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A number of polynuclear mixed carboxylates of nickel(II) with the general composition $[Ni(OOCCH_3)_{2-n}(OOCR')_n]_x$ (where $R' = C_{13}H_{27}$, $C_{15}H_{31}$, $C_{17}H_{35}$ and $C_{21}H_{43}$ and $n = 1$ or 2) have been synthesized by the transacylation reactions of anhydrous nickel acetate with higher carboxylic acids in refluxing toluene. On recrystallization from benzene—alcohol mixtures, mono-alcoholate complexes, $Ni(OOCCH_3)_{2-n}(OOCR')_n \cdot ROH$ (where $R = CH_3$ and C_2H_5) have been isolated. All these derivatives have been characterized by the molecular weight determinations, infra-red and electronic reflectance spectra and magnetic susceptibility measurements.

[Keywords: IR Spectra; Magnetic susceptibility measurements; Carboxylates, Ni(II); *Nickel*(II)*-carboxylates; UV Spectra]*

Synthese und Eigenschaften einiger gemischter Carboxylat-Komplexe von Nickel(II)

Komplexe des Typs $[Ni(OOCCH_3)_{2-n}(OOCR')_n]_x$ (mit $R' = C_{13}H_{27}$, $C_{15}H_{31}$, $C_{17}H_{35}$ und $C_{21}H_{43}$, $n = 1$ oder 2) wurden aus wasserfreiem Nickelacetat mit höheren Carbonsäuren in siedendem Toluol erhalten. Bei der Kristallisation aus Benzol—Alkohol-Mischungen wurden Monoalkoholate $Ni(OOCCH_3)_{2-n}(OOCR')_n \cdot ROH$ (mit $R = CH_3$ und C_2H_5) isoliert. Die Charakterisierung der Komplexe erfolgte mittels Molekulargewichtsbestimmung, Infrarot- und Elektronenspektren und der Messung der magnetischen Susceptibilität.

Introduction

Acetates and haloacetates of a number of transition metals (chromium, manganese, iron, cobalt, nickel, copper and zinc) have been widely investigated[1–3] for their various physical and structural properties. These acetates and haloacetates show a strong tendency to undergo addition reactions[4] with various oxygen and nitrogen donor ligands to form coordination complexes with interesting structural properties. However, substitution reactions of transition metal acetates

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have received very little attention. In the present paper, we report nickel(II) acetate to undergo substitution reactions with higher carboxylic acids resulting in the formation of mixed acetate higher carboxylates of nickel(II). After recrystallization in benzene-alcohol mixtures, alcoholate complexes of the derivatives have been isolated. All these derivatives have been characterized by infrared, electronic reflectance spectra, magnetic moments and molecular weight measurements with a view to throw light on the structures of these derivatives.

Results and Discussion

Transacylation reactions of anhydrous nickel acetate with higher carboxylic (myristic, palmitic, stearic and behenic) acids have been carried out in different stoichiometric ratios in refluxing toluene:

$$\mathrm{Ni(OOCCH_3)_2} + R\mathrm{COOH} \xrightarrow{\text{Toluene}} \mathrm{Ni(OOCCH_3)(OOC}R\mathrm{)} + \mathrm{CH_3COOH}\uparrow$$

$$\mathrm{Ni(OOCCH_3)_2} + 2\,R\mathrm{COOH} \xrightarrow{\text{Toluene}} \mathrm{Ni(OOC}R\mathrm{)_2} + 2\,\mathrm{CH_3COOH}\uparrow$$

(where $R = \mathrm{C_{13}H_{27}}$, $\mathrm{C_{15}H_{31}}$, $\mathrm{C_{17}H_{35}}$ and $\mathrm{C_{21}H_{43}}$)

Toluene forms an azeotrope (b.p.'s of the azeotrope and toluene are 106° and 110 °C respectively) with acetic acid. The use of toluene as a solvent makes it possible to carry out the above reactions in 1:1 as well as 1:2 molar ratios, as the acetic acid liberated during the course of the reactions can be removed azeotropically. The reactions are found to be facile and their progress could be followed by the estimation of the acetic acid content in the azeotrope collected. Mono- as well as disubstituted products have been obtained in quantitative yields. All these disoaps as well as mixed soaps are soluble in toluene and benzene. The solubility of mixed soap derivatives, $\mathrm{Ni(OOCCH_3)(OOC}R\mathrm{)}$, shows that these products are not equimolar mixtures of $\mathrm{Ni(OOCCH_3)_2}$ and $\mathrm{Ni(OOC}R\mathrm{)_2}$ as the former one is insoluble in common organic solvents. The identity of these products is further affirmed by their repeated crystallization. It may be emphasized that transacylation method appears to be particularly suited for the synthesis of mixed carboxylate derivatives of nickel(II) which can not be so easily synthesized by any other route.

All the derivatives isolated during the present investigations are non-volatile coloured solids and are soluble in benzene and insoluble in alcohols. The derivatives are, therefore, precipitated by adding alcohol (methanol or ethanol) to their benzene solution. On recrystallization from benzene—alcohol mixture, adducts with the formula, $\mathrm{Ni(OOCCH_3)_{2-n}\,(OOC}R'\mathrm{)_n \cdot} R\mathrm{OH}$ ($n = 1$ or 2) are obtained. These

Table 1. *Reaction products of nickel acetate and carboxylic acids*

S. No.	Reactants (g)	Molar Ratio	Product	Acetic acid in azeotrope (g) Found (Calcd.)	Nickel analysis (%) Found (Calcd.)	M. Wt.* Found (Calcd.)
1.	$Ni(OOCCH_3)_2$ + $C_{13}H_{27}COOH$ (3.26) (4.23)	1:1	$Ni(OOCCH_3)(OOCC_{13}H_{27})$ green solid	1.02 (1.10)	16.93 (17.01)	1,060 (345)
2.	$Ni(OOCCH_3)_2$ + $C_{13}H_{27}COOH$ (1.74) (4.46)	1:2	$Ni(OOCC_{13}H_{27})_2$ green solid	1.12 (1.18)	11.39 (11.43)	1,502 (513)
3.	$Ni(OOCCH_3)_2$ + $C_{15}H_{31}COOH$ (2.89) (4.22)	1:1	$Ni(OOCCH_3)(OOCC_{15}H_{31})$ green solid	0.96 (0.98)	15.67 (15.73)	1,149 (373)
4.	$Ni(OOCCH_3)_2$ + $C_{15}H_{31}COOH$ (1.16) (3.38)	1:2	$Ni(OOCC_{15}H_{31})_2$ light green solid	0.74 (0.79)	10.21 (10.30)	1,676 (570)
5.	$Ni(OOCCH_3)_2$ + $C_{17}H_{35}COOH$ (1.77) (2.84)	1:1	$Ni(OOCCH_3)(OOCC_{17}H_{35})$ dark green solid	0.59 (0.60)	14.54 (14.63)	—
6.	$Ni(OOCCH_3)_2$ + $C_{17}H_{35}COOH$ (1.84) (5.92)	1:2	$Ni(OOCC_{17}H_{35})_2$ yellowish green solid	1.20 (1.25)	9.41 (9.38)	—
7.	$Ni(OOCCH_3)_2$ + $C_{21}H_{43}COOH$ (2.60) (5.01)	1:1	$Ni(OOCCH_3)(OOCC_{21}H_{43})$ green solid	0.85 (0.88)	12.77 (12.83)	—
8.	$Ni(OOCCH_3)_2$ + $C_{21}H_{43}COOH$ (1.22) (4.72)	1:2	$Ni(OOCC_{21}H_{43})_2$ dark green solid	0.81 (0.82)	7.89 (7.96)	—

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* In 20 ml chloroform.

Table 2. *Recrystallised products of nickel(II) carboxylates*

S. No.	Compound	Solvent	Product	Analyses (%) Found(Calcd.)		Mol. Wt.* Found (Calcd.)
				Nickel	Alcohol	
1.	$Ni(OOCCH_3)(OOCC_{13}H_{27})$	*Me*OH	$Ni(OOCCH_3)(OOCC_{13}H_{27})\cdot \mathit{Me}OH$ light green solid	15.49 (15.56)	8.38 (8.50)	780 (377)
2.	$Ni(OOCCH_3)(OOCC_{15}H_{31})$	*Me*OH	$Ni(OOCCH_3)(OOCC_{15}H_{31})\cdot \mathit{Me}OH$ light green solid	14.41 (14.49)	7.71 (7.91)	826 (405)
3.	$Ni(OOCCH_3)(OOCC_{17}H_{35})$	*Et*OH	$Ni(OOCCH_3)(OOCC_{17}H_{35})\cdot \mathit{Et}OH$ light green solid	13.16 (13.12)	10.22 (10.30)	—
4.	$Ni(OOCCH_3)(OOCC_{21}H_{43})$	*Et*OH	$Ni(OOCCH_3)(OOCC_{21}H_{43})\cdot \mathit{Et}OH$ light green solid	11.56 (11.66)	9.06 (9.15)	—
5.	$Ni(OOCC_{15}H_{31})_2$	*Et*OH	$Ni(OOCC_{15}H_{31})_2\cdot \mathit{Et}OH$ green solid	9.48 (9.54)	7.42 (7.49)	1,206 (616)
6.	$Ni(OOCC_{17}H_{35})_2$	*Me*OH	$Ni(OOCC_{17}H_{35})_2\cdot \mathit{Me}OH$ light green solid	8.88 (8.93)	4.72 (4.88)	1,343 (658)
7.	$Ni(OOCC_{21}H_{43})_2$	*Me*OH	$Ni(OOCC_{21}H_{43})_2\cdot \mathit{Me}OH$ light green solid	7.56 (7.62)	4.21 (4.17)	—

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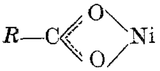
* In 20 ml chloroform.

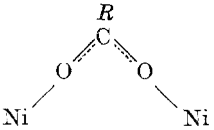
alcoholate complexes are also soluble in benzene but insoluble in alcohols. The addition molecule of alcohol appears to be lost at ~ 110 °C/1.0 mm pressure leaving the mixed as well as dicarboxylate derivatives of nickel in pure state.

Infrared Spectra

Infrared spectra of all the derivatives, $Ni(OOCCH_3)_{2-n}(OOCR')_n$ and their alcohol adducts were recorded in the range 4,000–200 cm^{-1} with CsI pellets. In the spectra of all the derivatives (except alcoholate derivatives), no band was observed in the region 3,600–3,200 cm^{-1} indicating complete absence of O—H stretching vibrations[5]. A strong band due to O—H deformation vibrations, which appears at ~ 935 cm^{-1} in the spectra of free carboxylic acids, was also found missing in the spectra of above derivatives. The carbonyl C=O stretching vibrations expected around 1,700 cm^{-1} were also found completely absent in the spectra of all the above derivatives indicating that carbonyl oxygen of COO group is coordinated giving either bidentically chelated



or bridged



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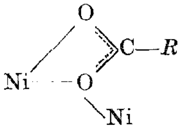

polymeric structures indicated above.

Though detailed infrared spectral studies have been carried out to distinguish the different modes of coordination in metal acetate complexes[6,7], no sharp line seems available to catagorise these on the basis of C—O stretching frequencies. However, *Nakamura*[8] has revealed the relative differences between the bidentate and bridging type of coordination by taking C—O vibrations in consideration. He suggested that in bridging structure OCO angle increases relative to that in bidentate ones consequently antisymmetric C—O stretching frequency is expected to increase.

In the present case the antisymmetric and symmetric C—O stretching frequencies have been observed at ~ 1,560 cm^{-1} and ~ 1,460 cm^{-1} respectively. Molecular weight determinations have revealed the $Ni(OOCCH_3)(OOCR')$, $Ni(OOCR')_2$ to be trimeric and their alcoholate adducts to be dimeric respectively. Electronic reflectance spectra also

Table 3. *Electronic spectra* and magnetic moments of carboxylate derivatives of nickel(II)*

S. No.	Compound	$^3A_{2g} \rightarrow {}^3T_{2g}$ (10 *Dq*)	$^3A_{2g} \rightarrow {}^3T_{1g}$(F) ($\nu_2$)	$^3A_{2g} \rightarrow {}^3T_{1g}$(P) ($\nu_3$)	*B*	β	μ_{eff} (*B.M.*)
1.	$Ni(OOCCH_3)(OOCC_{13}H_{27})$	8,772	14,925	24,690	886	0.85	3.23
2.	$Ni(OOCC_{13}H_{27})_2$	8,930	15,015	23,530	784	0.75	3.22
3.	$Ni(OOCCH_3)(OOCC_{15}H_{31})$	8,810	14,815	24,875	884	0.85	3.24
4.	$Ni(OOCC_{15}H_{31})_2$	9,010	14,880	23,810	777	0.74	3.26
5.	$Ni(OOCCH_3)(OOCC_{17}H_{35})$	8,810	14,706	25,125	893	0.86	3.26
6.	$Ni(OOCC_{17}H_{35})_2$	9,010	14,750	23,923	776	0.74	3.35
7.	$Ni(OOCCH_3)(OOCC_{21}H_{43})$	8,850	14,600	25,316	891	0.86	3.27
8.	$Ni(OOCC_{21}H_{43})_2$	9,090	14,600	24,510	790	0.76	3.31
9.	$Ni(OOCCH_3)(OOCC_{13}H_{27}) \cdot MeOH$	8,810	14,815	25,000	892	0.86	3.25
10.	$Ni(OOCCH_3)(OOCC_{15}H_{31}) \cdot MeOH$	8,850	14,750	26,315	900	0.86	3.27
11.	$Ni(OOCC_{15}H_{31})_2 \cdot EtOH$	9,050	14,706	25,330	740	0.71	3.25
12.	$Ni(OOCCH_3)(OOCC_{17}H_{35}) \cdot EtOH$	8,889	14,925	24,690	683	0.83	3.29
13.	$Ni(OOCC_{17}H_{35})(OOCC_{21}H_{43}) \cdot EtOH$	8,930	14,815	24,690	848	0.81	3.30
14.	$Ni(OOCC_{17}H_{35})_2 \cdot MeOH$	9,050	14,600	24,390	789	0.76	3.32
15.	$Ni(OOCC_{21}H_{43})_2 \cdot MeOH$	9,175	14,706	24,272	763	0.73	3.34

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

reveal that nickel is situated in an octahedral environment in these derivatives. On the basis of above data, intermolecular association appears to take place throught the bidentate carboxylic groups with carbonyl oxygen triply coordinated between two metal atoms.

Electronic Spectra and Magnetic Moments

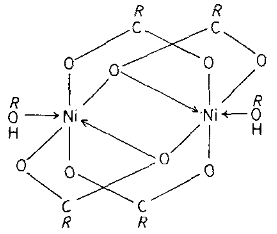
Electronic spectra of all the above carboxylate derivatives have been recorded in the range 4,000-28,000 cm^{-1} in nujol mulls or in chloroform and no marked difference could be observed in their spectra. The spectra are typical of divalent nickel atoms in an octahedral environment[9] which exhibit three absorption bands $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ observed at 8,000-10,000 (ν_1), 14,000-16,000 (ν_2) and 23,000-26,000 cm^{-1} (ν_3) respectively. The position of the bands, the proposed assignments, the ligand field parameters (Dq), the *Racah* parameters (B) and the covalency factors (β) are listed in Table 3. The parameter B has been calculated by the method of *Underhill* and *Billing*[10]. The values of B fall in the range 740-900 cm^{-1} which are much lower than 1,041 cm^{-1} (observed for free ion) showing appreciable covalent nature of the metal ligand bonds in these carboxylate derivatives.

Magnetic moments of all these derivatives have been measured at the room temperature and the results (Table 3) indicate that all the complexes show a magnetic moment in the range 3.22-3.35 *B. M.* which are in the range typical for nickel(II) in the high spin configuration of an octahedral environment. These values are higher compared to a "spin-only" value of 2.83 *B. M.* for a d^8 system. This may be due to the orbital contribution and the ferromagnetic interaction in the cluster[11].

Molecular Weight and Probable Structure

Molecular weights of the above carboxylate derivatives have been determined ebullioscopically in refluxing chloroform and the values obtained are presented in Tables 1 and 2. The results show that nickel mixed carboxylates, $Ni(OOCCH_3)(OOCR')$ as well as dicarboxylates, $Ni(OOCR')$ are trimeric while their alcohol adducts are dimeric in refluxing chloroform.

Both the magnetic and spectral studies suggest that the nickel atoms in all the above derivatives are situated in an octahedral environment. The trimeric structure suggested for the nickel bis-acetylacetonate complex[12] appears to be most plausible for the above trimeric derivatives as in these complexes also there are four oxygen atoms per nickel atom. Nevertheless, much more direct experimental evidence would be necessary to reach a final conclusion about their stereochemistry. The following plausible structures may tentatively be suggested for the dimeric alcoholates of mixed carboxylates as well as dicarboxylates of nickel(II).



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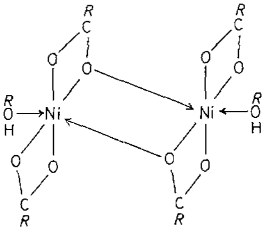

II

Experimental

All glass apparatus with interchangeable quickfit joints were used throughout. Extreme precautions were taken to exclude moisture. Carboxylic acids were used after distillation. Anhydrous nickel acetate was prepared by the reaction of nickel isoproxide (4.73 g) and acetic anhydride (5.46 g) in benzene (60 ml) under refluxing conditions.

Infrared spectra were recorded on a Perkin-Elmer 621 IR spectrophotometer. Visible reflectance spectra of solid complexes (in nujol mull) and in benzene solution were recorded on a Russian C Φ-10 recording spectrophotometer and near infrared spectra, on a Perkin-Elmer 4000 A. Molecular weights were determined in a semi-micro ebulliometer (Gallenkamp) with a thermister sensing device. Magnetic moment measurements were made at the room temperature by standard Gouy method in benzene solution.

Nickel was estamined gravimetrically as its dimethylglyoxime complex and alcohols by an oxidimetric method[13]. Acetic acid was estimated with standard sodium hydroxide solution, using phenolphthalein as indicator.

Reactions of Nickel Acetate with Higher Carboxylic Acids

To weighed amounts (~ 2 g) of nickel acetate suspended in toluene (70 ml) were added the required proportions of the carboxylic acids. Contents were refluxed at a bath temperature of 140-150 °C and acetic acid liberated was removed azeotropically with toluene (106 °C). After completion of reactions, the products were appeared to be highly soluble in toluene. The excess solvent was removed under reduced pressure (50 °C/0.6 mm) for 2 h. The experimental results are summarized in Table 1.

All the derivatives are soluble in benzene and insoluble in alcohols, therefore, these are precipitated by adding alcohol to a benzene solution. On heating again the precipitated products dissolved and on cooling, coloured crystals were obtained. These were dried *in vacuo* and coloured solids were obtained. Detailed experimental results are summarized in Table 2.

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