Trinuclear Intermediates Isolated in the Reactions of Bis(acetylacetonato)-nickel(II) with Dry Hydrogen Bromide

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The reactions of bis(acetylacetonato)nickel(II) with restricted amounts of dry hydrogen bromide have been performed in appropriate mixtures of dichloromethane and petroleum ether at room temperature or lower in order to isolate the intermediary products, $Ni_3Br(acac)_5$, $Ni_3Br_2(acac)_4$, and $Ni_3Br_4(acac)_2$. The essentially octahedral trinuclear structure of $Ni_3Br(acac)_5$ was established on the basis of elemental analysis, by molecular-weight and magnetic-moment determinations, and by studying the electronic and IR spectra. $Ni_3Br_2(acac)_4$ and $Ni_3Br_4(acac)_2$ were characterized less satisfactorily because of their lower solubilities. The reactions of these mixed complexes with pyridine have also been examined; a new complex $NiBr(acac)(py)_3$ was thus obtained in addition to the known compound, $Ni(acac)_2(py)_2$.

As an extension of our studies of the reactions of various metal acetylacetonate complexes with bromine,[1-6] we have examined the reaction between bis(acetylacetonato)nickel(II) and bromine in dichloromethane.[7] Bis(acetylacetonato)cobalt(II) is known to exist as a tetrameric molecule in crystals[8] and to be trimeric in non-coordinating solvents.[9,10] Oligomeric mixed cobalt(II) complexes containing bridging acetylacetonate anions, such as $Co_3(acac)_6(H_2O)$,[11] $Co_2(acac)_4(py)$,[10] and $Co_2(acac)_4L_2$, where L is water,[12] pyridine,[10] or cyclohexylamine,[13] have also been reported. In a reaction of bis(acetylacetonato)-cobalt(II) with an equimolar amount of bromine in dichloromethane at 0 °C, a dimeric mixed complex, $Co_2Br_2(acac)_2$, was isolated,[6] but no other tetrameric or trimeric intermediary compound has yet been identified.

The trimeric nature of anhydrous bis(acetylacetonato)nickel(II) has also been well established for crystals[14] and in non-donor solvents,[15] The relative stabilities of the trimeric structure of $M(acac)_2$ in non-coordinating solvents are considered to be in the following order:[16] Ni(II)>Co(II)>Mn(II)>Zn(II). Thus, the reaction of bis(acetylacetonato)nickel(II) with bromine was expected to afford some trinuclear intermediary products preserving the bridging acetylacetonate anions. In fact, novel mixed complexes, $Ni_3Br_2(acac)_4$ and $Ni_3Br_4(acac)_2$, were obtained by the reactions of $Ni_3(acac)_6$ with restricted amounts of bromine in dichloromethane.[7] In such reactions monobromoacetylacetone is also produced; it is neither volatile nor stable, and gives some trouble in the purification of intermediates. To avoid this difficulty, hydrogen bromide was employed in place of bromine. Acetylacetone is produced instead, but the general pattern of the reaction is the same as with bromine.[2,3]

In the reaction of bis(acetylacetonato)nickel(II) with dry hydrogen bromide in dichloromethane, another trinuclear intermediary product, $Ni_3Br(acac)_5$, was obtained.[17] This paper will report in detail on the isolation and characterization of these three trinuclear complexes.

Experimental

Materials. Bis(acetylacetonato)diaquonickel(II) prepared by the method of Charles and Pawlikowski[18] was recrystallized three times from methanol, and then dehydrated to anhydrous $Ni_3(acac)_6$ by heating it at 100 °C *in vacuo* for 4 hr (Found: Ni, 23.45; C, 45.63; H, 5.55%). Dichloromethane was purified and dried by the standard method.[19] Hydrogen bromide was generated by a reaction between tetraline and bromine, and was dissolved in purified dichloromethane.[2] Petroleum ether was distilled over metallic sodium, and a fraction distilled at 40—50 °C was used. For optical measurements, the petroleum ether was purified according to the method of Tonberg and Johnston.[20] Pyridine was freshly distilled before use.

Reactions of Bis(acetylacetonato)nickel(II) with Dry Hydrogen Bromide. Bis(acetylacetonato)nickel(II) was dissolved in a mixture of dichloromethane and petroleum ether in

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a three-necked flask equipped with a burette, a glass tube containing phosphorus pentoxide, and another glass tube connected to filtration equipment by means of polyethylene tubing. With vigorous magnetic stirring, a dichloromethane solution of hydrogen bromide (*ca.* 0.1 M) was gradually added from the burette. The precipitate thus formed was transferred *via* the polyethylene tubing to a vacuum filtration apparatus set up in a desiccator containing phosphorus pentoxide. When no precipitate was separated, the solvent was evaporated to some extent to obtain a precipitate.

If enough amount of hydrogen bromide is used, the ultimate product of the reaction is nickel(II) bromide (Found: Ni, 26.60; Br, 72.67%. Yield: 99%). However, when a restricted amount of hydrogen bromide is employed, three kinds of intermediary products are obtained, depending on the reactants' mole ratio. In each case, a mixed solvent containing appropriate portions of dichloromethane and petroleum ether was used to discriminate a desired intermediary product from other species.

Bromopentakis(acetylacetonato)trinickel(II), $Ni_3Br(acac)_5$. Two grams (2.6 mmol) of $Ni_3(acac)_6$ were dissolved in 200 ml of a mixture of dichloromethane and petroleum ether (1 : 10 by volume). Into this solution vigorously stirred, we then added, drop by drop, 26 ml of a dichloromethane solution of hydrogen bromide (2.6 mmol) from the burette. The solution was green throughout the reaction, showing no remarkable change. The solvent was evaporated up to about one fifth in volume, thus producing a green precipitate. Found: Ni, 23.21; Br, 10.24; C, 40.01; H, 4.86%. Calcd for $C_{25}H_{35}O_{10}BrNi_3$: Ni, 23.41; Br, 10.63; C, 39.91; H, 4.66%. Yield: 80%.

The $Ni_3(acac)_6$ reactant is highly soluble in dichloromethane and does not precipitate even when a solution of the same concentration as above is concentrated to one twentieth in volume. The possibility that the above reaction product may be a mixture of unreacted $Ni_3(acac)_6$ and some product can thus be rejected.

Dibromotetrakis(acetylacetonato)trinickel(II), $Ni_3Br_2(acac)_4$. (1) Two grams (2.6 mmol) of $Ni_3(acac)_6$ was dissolved in 100 ml of a mixture of dichloromethane and petroleum ether (2 : 15 by volume), and was then kept at $-5\sim-10$ °C by cooling with ice and salt. To this solution we then gradually added a 0.1 M solution of hydrogen bromide (5.2 mmol) in dichloromethane. After about 1.5 times as many moles of hydrogen bromide had been added, a yellow-green hygroscopic precipitate began to separate out. Found: Ni, 23.39; Br, 20.65; C, 32.05; H, 4.21%. Calcd for $C_{20}H_{28}O_8Br_2Ni_3$: Ni, 24.05; Br, 21.82; C, 32.77; H, 3.82%. Yield: 85%.

(2) Alternatively, 1.5 g (2 mmol) of $Ni_3Br(acac)_5$ was allowed to react with an equimolar amount of hydrogen bromide in dichloromethane–petroleum ether (1 : 1 by volume) at $-5\sim-10$ °C. A yellow green precipitate began to appear at about the middle of the overall reaction. The analytical data and infrared spectra of this product coincide completely with those of the specimen prepared in (1). Found: Ni, 23.00; Br, 20.90; C, 32.66; H, 4.38%. Yield: 92%.

Tetrabromobis(acetylacetonato)trinickel(II), $Ni_3Br_4(acac)_2$. (1) Two grams (2.6 mmol) of $Ni_3(acac)_6$ were dissolved in 40 ml of a mixture (1 : 3 by volume) of dichloromethane and petroleum ether. To this solution we then added a dichloromethane solution of four times as many moles of hydrogen bromide with cooling at $-5\sim-10$ °C. A very hygroscopic yellow powder precipitated; this powder turned brownish yellow on drying. Found: Ni, 25.45; Br, 50.21; C, 14.77; H, 2.20%. Calcd for $C_{10}H_{14}O_4Br_4Ni_3$: Ni, 25.37; Br, 48.91; C, 17.29; H, 2.01%. Yield: 95%.

(2) In 100 ml of a mixed solvent (7 : 3 by volume) of dichloromethane and petroleum ether, 1.5 g (2 mmol) of $Ni_3Br(acac)_5$ were allowed to react with three times as many moles of hydrogen bromide at $-5\sim-10$ °C. When about half the hydrogen bromide had been added, a yellow precipitate began to appear. Found: Ni, 24.41; Br, 49.10%. Yield: 93%.

The analytical data for $Ni_3Br_2(acac)_4$ and $Ni_3Br_4(acac)_2$ are very poor due to their very hygroscopic characters.

The Reaction of Bromopentakis(acetylacetonato)trinickel(II) with Pyridine. One gram (1.33 mmol) of $Ni_3Br(acac)_5$ was dissolved in 30 ml of dichloromethane. To this solution we then added, drop by drop, 15 ml of a dichloromethane solution containing 9.31 mmol of pyridine. The reaction mixture was kept standing for a week in a desiccator equipped with a glass tube containing calcium chloride. The solvent was thus vaporized almost to dryness. Two kinds of crystals resulted. Blue-violet crystals were dissolved in benzene, but other blue crystals remained insoluble and gave the following analysis. Found: Ni, 12.74; Br, 17.10; C, 50.98; H, 4.90; N, 8.66%. Calcd for $NiBr(acac)(py)_3=C_{20}H_{22}O_2N_3BrNi$: Ni, 12.36; Br, 16.82; C, 50.52; H, 4.63; N, 8.84%. Yield: 90% on the basis of Eq. (11), which will be shown in the Results and Discussion section. The benzene solution was evaporated to dryness, and the residue was recrystallized from methanol to give blue-violet crystals. Found: Ni, 14.46; C, 57.59; H, 5.85; N, 7.02%. Calcd for $Ni(acac)_2(py)_2=C_{20}H_{24}O_4N_2Ni$: Ni, 14.14; C, 57.81; H, 5.78; N, 6.74%. Yield of crystals: 60% on the basis of Eq. (11).

The Reaction of Dibromotetrakis(acetylacetonato)trinickel(II) with Pyridine. A dichloromethane solution (20 ml) of pyridine (5.44 mmol) was added, drop by drop, to a suspension of $Ni_3Br_2(acac)_4$ (0.5 g, 0.68 mmol) in dichloromethane (30 ml). The complex was dissolved gradually with an increase in the amount of pyridine added. The blue solution was kept standing for two days in an evacuated desiccator. The residue was extracted with benzene, and the remaining blue crystals were identified by the IR assay as $NiBr(acac)(py)_3$. Yield: 20% on the basis of Eq. (12). To the benzene extract, petroleum ether was added to separate an impure, pale green precipitate; the filtrate was evaporated to give blue violet crystals which were identified by the IR assay as $Ni(acac)_2(py)_2$. Yield: 65% on the basis of Eq. (12).

The Reaction of Tetrabromobis(acetylacetonato)trinickel(II) with Pyridine. A dichloromethane solution of excess pyridine was added to a dichloromethane suspension of $Ni_3Br_4(acac)_2$. A blue solution was concentrated by evaporation to give pale blue-green crystals. Found: Ni, 10.90; Br, 30.10; C, 44.34; H, 3.86; N, 10.32%. Calcd for $NiBr_2(py)_4=C_{20}H_{20}N_4Br_2Ni$: Ni, 10.98; Br, 29.88; C, 44.91; H, 3.77; N, 10.47%. Yield: 82% on the basis of Eq. (13). The filtrate was evaporated to dryness, and the residue was recrystallized from methanol to give blue-violet crystals of $Ni(acac)_2(py)_2$. Yield: 40% on the basis of Eq. (13).

Analysis and Measurements. All the solid samples were subjected to elemental analysis after drying *in vacuo* at room temperature. Nickel and bromine were determined gravimetrically as bis(dimethylglyoximato)nickel(II) and silver bromide respectively. To determine the concentration of hydrogen bromide in dichloromethane, an aqueous solution of sodium hydroxide was added to an aliquot of the hydrogen bromide solution, and the excess alkali was titrated with 0.1 N sulfuric acid, using phenolphthalein as an indicator.

The visible and ultraviolet absorption spectra were measured by means of a Hitachi EPS-3T autorecording spectro-

photometer. The molar absorption coefficients of trinuclear complexes are expressed on the basis of the gram-atom of nickel(II). The infrared spectra were taken in Nujol on JASCO IR-E (4000—700 cm^{-1}), Hitachi EPI-L (700—200 cm^{-1}), and FIS-3 (400—30 cm^{-1}) infrared spectrophotometers.

The magnetic susceptibility was measured at room temperature by the Gouy method by means of an automatically-recording magnetic balance (Shimadzu Seisakusho Co., Ltd.). Hexaamminechromium(III) chloride and mercury-(II) tetraisothiocyanatocobaltate(II) were used as the reference compounds.

The molecular weight was determined cryoscopically in benzene by means of an apparatus manufactured by Knauer, Germany. Tris(acetylacetonato)aluminium was used as the reference.

Results and Discussion

When six times as many moles of dry hydrogen bromide were allowed to react with $Ni_3(acac)_6$ in dichloromethane, anhydrous nickel(II) bromide precipitated in a 99% yield. The UV spectrum of the filtrate showed that six times as many moles of acetylacetone were produced in this reaction, certifying the following stoichiometry.

$$Ni_3(acac)_6 + 6HBr = 3NiBr_2 + 6acacH \quad (1)$$

Here, acacH stands for an acetylacetone molecule.

The overall reaction (1) must proceed *via* several consecutive steps, and it depends on the relative rates of these elementary steps whether or not some intermediary products can be isolated and characterized. Fortunately, the trinuclear framework of $Ni_3(acac)_6$ was strong enough, and the differences among the rates of the consecutive reaction steps were large enough, for three kinds of intermediary products to be isolated in satisfactory yields and purities. The reactions producing these mixed complexes may be represented by the following equations:

$$Ni_3(acac)_6 + HBr = Ni_3Br(acac)_5 + acacH \quad (2)$$

$$Ni_3Br(acac)_5 + HBr = Ni_3Br_2(acac)_4 + acacH \quad (3)$$

$$Ni_3Br_2(acac)_4 + 2HBr = Ni_3Br_4(acac)_2 + 2acacH \quad (4)$$

In principle, two more intermediates, $Ni_3Br_3(acac)_3$ and $Ni_3Br_5(acac)$, may be expected to be involved in the course of the conversion of $Ni_3(acac)_6$ to nickel(II) bromide. However, even the tribromo-intermediate could not be obtained. The reason for this is not clear, but $Ni_3Br_3(acac)_3$ might be especially unstable compared to $Ni_3Br_2(acac)_4$ and $Ni_3Br_4(acac)_2$.

The three isolated mixed complexes show a very remarkable trend in their properties. For instance, they show intermediate colors between the green of $Ni_3(acac)_6$ and the orange of nickel(II) bromide. $Ni_3Br(acac)_5$ is quite soluble in dichloromethane, but $Ni_3Br_2(acac)_4$ is much less soluble and $Ni_3Br_4(acac)_2$ is insoluble in the same solvent. The hygroscopic character is remarkably enhanced with an increase in the content of bromine.

Properties of $Ni_3Br(acac)_5$. As is shown in Table 1, the molecular weight determined cryoscopically in benzene indicates that this is a trinuclear complex. The ultraviolet absorption spectrum in Fig. 1 and the visible absorption spectrum in Fig. 2 also support the trinuclear and essentially octahedral structure of this compound. The ultraviolet spectra of bis(acetylacetonato)nickel(II) in dry dichloromethane have recently been reinvestigated in detail;[21] the more intense absorption band at 265 nm has been attributed to the trinuclear molecule, while the low-energy band at 300 nm has been attributed to the mononuclear dihydrated species. The high-energy band of Curve 2

Table 1. Molecular weights of $Ni_3(acac)_6$ and $Ni_3Br(acac)_5$ determined cryoscopically in benzene

Concn, M	$Ni_3(acac)_6$	Concn, M	$Ni_3Br(acac)_5$
0.0991	780	0.0792	750
0.0496	728	0.0396	717
0.0248	764	0.0198	747
Average	757	Average	738
Theoretical	771	Theoretical	752

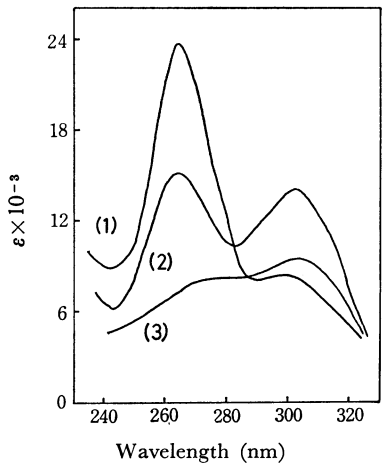


Fig. 1. The ultraviolet absorption spectra of $Ni_3(acac)_6$ (curve 1), $Ni_3Br(acac)_5$ (curve 2), and $Ni_3Br_2(acac)_4$ (curve 3) in dichloromethane.

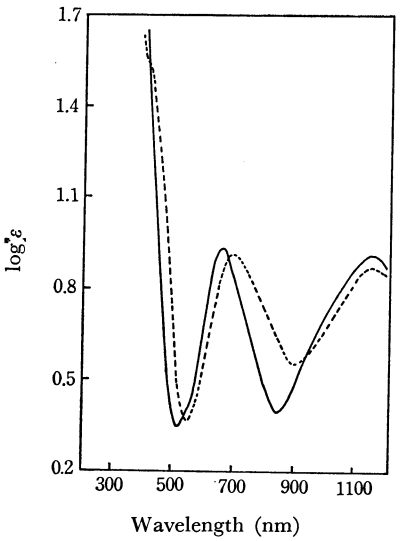


Fig. 2. The visible absorption spectra of $Ni_3(acac)_6$ (——) and $Ni_3Br(acac)_5$ (----) in dichloromethane.

in Fig. 1 indicates the existence of the trinuclear framework in $Ni_3Br(acac)_5$.

The visible absorption spectrum of $Ni_3(acac)_6$ in dichloromethane shows two maxima, at 1150 (ε=8.2) and 660 nm (ε=8.5), closely resembling the pattern in cyclohexane reported by Cotton and Fackler.[15b] The spectrum of $Ni_3Br(acac)_5$ also has two maxima, at 1140 (ε=7.4) and 695 nm (ε=8.2), revealing the essentially octahedral environment of the nickel(II) ion in this compound. The observed effective magnetic moment of 3.51 B.M. also indicates the high-spin state of the nickel(II) ion.

In order for $Ni_3Br(acac)_5$ to exist as a discrete trinuclear molecule, one of the three nickel ions must assume a pentacoordinate structure. In other words, it seems probable that one of the non-bridging acetylacetonate groups in $Ni_3(acac)_6$ was displaced by a bromide anion. The shoulder observed at 405 nm (Fig. 2) might reflect the five-coordinate nickel(II).[22] In fact, the shoulder disappeared on the addition of equimolar pyridine to the solution of $Ni_3Br(acac)_5$, presumably because of the completion of the totally octahedral structure.

As is shown in Fig. 3, the infrared spectrum of $Ni_3Br(acac)_5$ is much more complicated than that of $Ni_3(acac)_6$, suggesting the poorer symmetry of the former compound. Such a spectral feature also supports the above structural consideration.

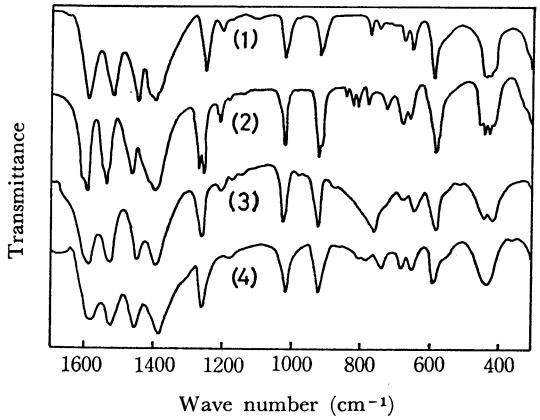


Fig. 3. The infrared absorption spectra in Nujol mull of $Ni_3(acac)_6$ (curve 1), $Ni_3Br(acac)_5$ (curve 2), $Ni_3Br_2(acac)_4$ (curve 3), and $Ni_3Br_4(acac)_2$ (curve 4).

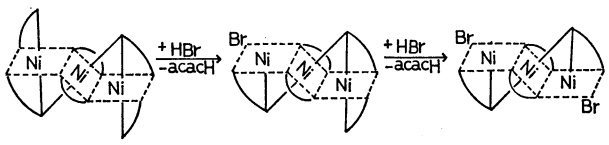
$Ni_3Br_2(acac)_4$ and $Ni_3Br_4(acac)_2$. The lower solubilities of these dibromo and tetrabromo complexes in the appropriate solvents prevented the molecular-weight determination. The ultraviolet spectrum of $Ni_3Br_2(acac)_4$ (Curve 3 in Fig. 1) has a broad band at 260—280 nm, indicating the maintenance of the trinuclear framework.

In a previous paper,[21] the peak-height ratio of the high-energy to low-energy bands for bis(acetylacetonato)nickel(II) was found to decrease with an increase in the water content of dichloromethane due to the depolymerization equilibrium:

$$Ni_3(acac)_6 + 6H_2O \rightleftharpoons 3Ni(acac)_2(H_2O)_2 \quad (5)$$

Although the three spectra in Fig. 1 were taken in dichloromethane of almost same water content (*ca.* 4.5×10^{-3} M), the low-energy band grows at the expense of the high-energy band as the bromine content of the mixed complex increases. A depolymerization equilibrium similar to (5) might be more favorable for $Ni_3Br(acac)_5$ than for $Ni_3(acac)_6$, and more favorable for $Ni_3Br_2(acac)_4$ than for $Ni_3Br(acac)_5$.

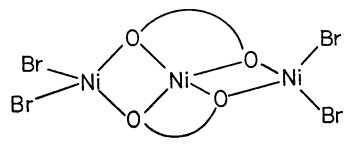
The effective magnetic moment of $Ni_3Br_2(acac)_4$ (3.38 B.M.) is appreciably lower than that, 3.51 B.M., for $Ni_3Br(acac)_5$; it is rather near to that, 3.37 B.M., for $Ni_3(acac)_6$. In the previous section it was presumed that a non-bridging acetylacetonate ligand was displaced by the attack of hydrogen bromide (Eq. (2)). If this presumption be extended to the second step of the reaction (Eq. (3)), another non-bridging acetylacetonate group will be displaced, as is illustrated by Eq. (6).



(6)

In order for $Ni_3Br_2(acac)_4$ to retain the trinuclear structure, both terminal nickel(II) ions must be in the five-coordinate environment. Of course, it is not at all clear whether a square-pyramidal or a trigonal-bipyramidal structure is preferred. The infrared spectrum of $Ni_3Br_2(acac)_4$ (Curve 3 in Fig. 3) is much simpler than that of $Ni_3Br(acac)_5$ and rather resembles that of $Ni_3(acac)_6$, indicating that the symmetry of $Ni_3Br_2(acac)_4$ is higher than that of $Ni_3Br(acac)_5$. It is very unfortunate that the visible absorption spectrum of $Ni_3Br_2(acac)_4$, which might exhibit the characteristic feature of the five-coordinate nickel(II), can not be observed because of its low solubility.

The tetrabromo-complex $Ni_3Br_4(acac)_2$ is more hygroscopic than $Ni_3Br_2(acac)_4$, and its low solubility in nondonor solvents prevented satisfactory characterization. The infrared spectrum of $Ni_3Br_4(acac)_2$ (Curve 4 in Fig. 3) is rather simple, resembling that of $Ni_3(acac)_6$. In order to retain the trinuclear structure, all three nickel(II) ions in $Ni_3Br_4(acac)_2$ must be in the four-coordinate environment. The observed paramagnetism (μ_{eff}=3.33 B.M.) clearly shows the square-planar arrangement to be impossible. Thus a tetrahedral structure such as the following may be imagined:



Adduct Formations. A methanolic solution of bis(acetylacetonato)nickel(II) shows an absorption maximum at 295 nm, accompanied by a shoulder on the longer-wavelength side. Cotton and Fackler[15b] presumed that the solute is entirely present as the sol-

21) K. Isobe, Y. Nakamura, and S. Kawaguchi, This Bulletin, **46**, 166 (1973).

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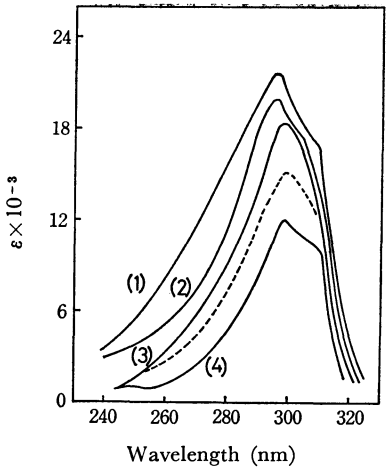

Fig. 4. The ultraviolet absorption spectra in methanol of $Ni_3(acac)_6$ (curve 1, $\lambda_{max}=295$ nm, $\varepsilon=21710$), $Ni_3Br(acac)_5$ (curve 2, $\lambda_{max}=295$ nm, $\varepsilon=19818$), $Ni_3Br_2(acac)_4$ (curve 3, $\lambda_{max}=299$ nm, $\varepsilon=18560$), and $Ni_3Br_4(acac)_2$ (curve 4, $\lambda_{max}=299$ nm, $\varepsilon=11952$). A dashed curve is a spectrum calculated for a presumed species $NiBr(acac)(CH_3OH)_3$ ($\lambda_{max}=300$ nm, $\varepsilon=15885$).

vated species, $Ni(acac)_2\cdot 2CH_3OH$, which was recently prepared by the reaction of $Ni_3(acac)_6$ with methanol in petroleum ether.[21]

Fig. 4 shows the ultraviolet absorption spectra of bis(acetylacetonato)nickel(II) and of three bromo-complexes derived therefrom. All these spectra show quite a striking resemblance to each other except that the apparent molar extinction coefficient decreases with the decrease in the acetylacetonate anions involved. These spectral features clearly indicate that the trinuclear mixed complexes are also depolymerized in such a coordinating solvent, just as $Ni_3(acac)_6$ is. In analogy with Eq. (5), these reactions might be represented by the following equations:

$$Ni_3(acac)_6 + 6CH_3OH = 3Ni(acac)_2(CH_3OH)_2 \quad (7)$$

$$Ni_3Br(acac)_5 + 7CH_3OH = 2Ni(acac)_2(CH_3OH)_2 + NiBr(acac)(CH_3OH)_3 \quad (8)$$

$$Ni_3Br_2(acac)_4 + 8CH_3OH = Ni(acac)_2(CH_3OH)_2 + 2NiBr(acac)(CH_3OH)_3 \quad (9)$$

$$Ni_3Br_4(acac)_2 + 10CH_3OH = Ni(acac)_2(CH_3OH)_2 + 2NiBr_2(CH_3OH)_4 \quad (10)$$

The presumed complex, $NiBr(acac)(CH_3OH)_3$, has not yet been isolated, but its spectrum can be calculated from Curves 1 and 2 or from Curves 1 and 3 in Fig. 4. These two calculated spectra are very close to each other; an averaged curve is drawn in Fig. 4.

In order to study such depolymerization (adduct formation) reactions more precisely, the reactions of these trinuclear complexes with pyridine were examined in dichloromethane. As has been described in the Experimental section, addition products reconciled with the following equations were obtained in satisfactory yields:

$$Ni_3Br(acac)_5 + 7py = 2Ni(acac)_2(py)_2 + NiBr(acac)(py)_3 \quad (11)$$

$$Ni_3Br_2(acac)_4 + 8py = Ni(acac)_2(py)_2 + 2NiBr(acac)(py)_3 \quad (12)$$

$$Ni_3Br_4(acac)_2 + 10py = Ni(acac)_2(py)_2 + 2NiBr_2(py)_4 \quad (13)$$

The fact that $Ni_3Br(acac)_5$ gave $NiBr(acac)(py)_3$ in the reaction with pyridine supports the assumption that $Ni_3Br(acac)_5$ contains a five-coordinate nickel(II). Furthermore, the fact that $Ni_3Br_2(acac)_4$ also produced $NiBr(acac)(py)_3$ and not $NiBr_2(py)_4$ clearly indicates that the two bromine atoms are linked to different nickel atoms in $Ni_3Br_2(acac)_4$ in accordance with the formula in Eq. (6).

Bis(acetylacetonato)bis(pyridine)nickel(II) was identified by elemental analysis and by comparing the IR and electronic spectra with those in the literature.[23,24] Dibromotetrakis(pyridine)nickel(II) is also a known compound; it was identified by elemental analysis and studying its IR spectrum.[25] On the contrary, bromo(acetylacetonato)tris(pyridine)nickel(II) $NiBr(acac)(py)_3$ is a new compound. In Fig. 5, the infrared spectrum in the 100—700 cm^{-1} region is compared with that of $Ni(acac)_2(py)_2$. A combination band at 574 cm^{-1} which was previously assigned to ν(Ni–O) and ring vibrations in $Ni(acac)_2(py)_2$[24] is replaced by two peaks, at 571 and 557 cm^{-1}, in $NiBr(acac)(py)_3$, indicating weaker Ni–O bonding and poorer symmetry in the latter complex. The ν(Ni–O)+ν(CR) at 438 cm^{-1} in the former complex is also shifted to 433 cm^{-1} in the latter; a similar feature is also observed in the 200—300 cm^{-1} region. Three strong peaks are observed at 262, 247, and 235 cm^{-1} for $NiBr(acac)(py)_3$ instead of the ν (Ni–O) and ν(Ni–N) bands at 272 and 250 cm^{-1} in $Ni(acac)_2(py)_2$. It is not certain whether or not one of the three peaks in the former complex should be assigned to the ν(Ni–Br) vibration, although no other strong peak attributable to ν (Ni–Br) is noticed.

Supplemental Discussion. Fackler[26] prepared

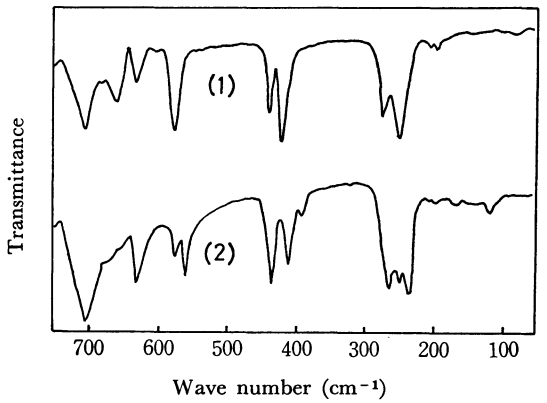

Fig. 5. The infrared spectra in Nujol mull of $Ni(acac)_2(py)_2$ (curve 1) and $NiBr(acac)(py)_3$ (curve 2).

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tetrakis(acetylacetonato)pyridinedinickel(II) $Ni_2(acac)_4py$ by the reaction of $Ni_3(acac)_6$ with a restricted amount of pyridine in benzene. Bertrand *et al.* synthesized $Ni(acac)(OCH_3)(CH_3OH)$ by the reaction of $Ni_3(acac)_6$ with equimolar potassium hydroxide in refluxing methanol. This compound is tetrameric in chloroform and is isostructural with $[Co(acac)(OCH_3)(CH_3OH)]_4$, which takes a cubane-type structure.[27] However, no derivative retaining the trinuclear framework of $Ni_3(acac)_6$ has yet been reported except $Ni_3OH(acest)_5$ which was obtained by Hay and Hook[28] in the reaction between the aqueous nickel(II) ion and ethyl acetoacetate (acestH) in the presence of potassium hydroxide or ammonia. The trinuclear octahedral structure of this compound was established by the cryoscopic and spectral measurements in benzene; an OH-bridged structure was presumed on the basis of the very sharp OH stretching band at 3587 cm^{-1} and the preliminary NMR data in benzene. $Ni_3Br(acac)_5$ prepared in the present study might have a structure similar to that of this ester complex, but the possibility of a bromide-bridging contrary to the proposed structure in Eq. (6) can not be denied. The conclusive description of the molecular structures of these trinuclear mixed complexes must await X-ray studies.

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