This finding would suggest that π-electron interactions are also an important factor in clathrate formation and recent findings in other laboratories[8] support the concept of a "sandwich-type" interaction in these Werner-type complex clathrates.

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Bis Adducts of Some Long-Chained Primary Alkyl- and Alkenylamines with the Acetylacetonates of Cobalt(II) and Nickel(II)

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Numerous preparations of adducts of N donors with metal β-diketonates have been reported.[1] Hashagen and Fackler[2] reported the preparation of bis adducts of some β-diketonates of cobalt(II) and nickel(II) with several primary amines, including *n*-propylamine and *n*-butylamine. The *n*-butylamine adduct of nickel(II) acetylacetonate was also prepared by Olszewski and Martin.[3] We were interested in seeing if the chain length of the coordinated amines could be extended beyond four carbon atoms to produce complexes of unusual dimensions; we were also interested in the effect of chain length on physical properties and in the effect of the presence of unsaturation in the hydrocarbon chain. We report the preparation of adducts of bis(acetylacetonato)cobalt(II) and -nickel(II) with primary alkylamines containing six, eight, eleven, thirteen, fourteen, and sixteen carbon atoms. We also report the preparation of adducts of the same metal chelates with unsaturated primary amines containing three, eleven, and eighteen carbon atoms; these amines include allylamine (1-amino-2-propene), undecenylamine (1-amino-10-hendecene), oleylamine (1-amino-9-octadecene), and linoleylamine (1-amino-8,11-octadecadiene).

Experimental Section

Preparation of the Adducts.—The bis acetylacetonates of cobalt(II) and nickel(II) were obtained from Alfa Inorganics. The amines were obtained from various commercial sources, except for undecenylamine, which was prepared by the Gabriel synthesis from undecylenyl bromide and potassium phthalimide followed by hydrolysis of the *N*-undecylenyl phthalimide.

The adducts with the saturated amines, and with allylamine, were prepared by addition of amine in excess of the calculated 2:1 molar ratio to hot benzene or toluene solutions of the metal acetylacetonate. A voluminous precipitate formed, which became a gelatinous mass upon cooling. The precipitate was filtered out by suction, washed with solvent, recrystallized from dimethylformamide, washed with *n*-pentane, and air dried. The allylamine complexes are obtained as fine needles. The complexes with saturated amines are obtained as fibrous, flaky solids. They are smooth and slippery to the touch and tend to pick up electrostatic charge from the air. The cobalt complexes are light orange and the nickel complexes light blue; the colors become paler as the chain length of the amine increases.

TABLE I
ADDUCTS OF TYPE $M(acac)_2(am)_2$[a]

Complex	Mp, °C	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found	μ_{eff},[b] BM
$Co(acac)_2(nha)_2$	139–140	57.49	57.56	9.66	10.06	6.10	5.84	4.8
$Co(acac)_2(noa)_2$	137–138	60.54	61.35	10.18	9.80	5.43	5.59	4.9
$Co(acac)_2(nua)_2$	132–133	64.07	63.95	10.78	10.52	4.67	4.67	4.8
$Co(acac)_2(trda)_2$	128–129	65.91	65.76	11.08	11.13	4.27	4.02	...
$Co(acac)_2(ttda)_2$	123–125	66.72	66.36	11.22	11.50	4.09	3.85	...
$Co(acac)_2(hda)_2$	122–123	68.15	65.26	11.44	11.01	3.78	3.39	4.8
$Co(acac)_2(aa)_2$	127–130	51.75	51.48	7.62	7.70	7.54	7.39	4.8
$Co(acac)_2(uena)_2$	116–118	64.50	63.44	10.15	10.12	4.70	4.63	...
$Co(acac)_2(ola)_2$	108–110	69.75	69.03	11.20	11.14	3.54	3.74	4.8
$Co(acac)_2(lla)_2$	106–107	70.10	70.05	10.74	10.62	3.55	3.54	...
$Ni(acac)_2(nha)_2$	150–152	57.42	58.45	9.67	9.86	6.10	6.20	3.3
$Ni(acac)_2(noa)_2$	148–150	60.57	60.80	10.19	9.92	5.43	5.25	3.4
$Ni(acac)_2(nua)_2$	149–151	64.09	64.83	10.78	11.43	4.67	4.34	3.4
$Ni(acac)_2(trda)_2$	148–149	65.93	65.36	11.09	11.31	4.27	4.45	...
$Ni(acac)_2(ttda)_2$	143–144	66.74	66.90	11.22	11.59	4.09	3.95	...
$Ni(acac)_2(hda)_2$	139–141	68.18	68.03	11.44	11.36	3.78	3.55	3.3
$Ni(acac)_2(aa)_2$	147–149	51.78	52.03	7.63	7.51	7.55	7.67	3.2
$Ni(acac)_2(uena)_2$	141–143	64.52	67.10	10.15	10.16	4.70	4.47	...
$Ni(acac)_2(ola)_2$	130–132	69.77	70.05	11.20	10.65	3.54	3.52	3.2
$Ni(acac)_2(lla)_2$	120–123	70.12	69.75	10.75	11.05	3.56	3.67	...

[a] Abbreviations: acac, acetylacetonate; am, amine; nha, *n*-hexylamine; noa, *n*-octylamine; nua, *n*-undecylamine; trda, *n*-tridecylamine; ttda, *n*-tetradecylamine; hda, *n*-hexadecylamine; aa, allylamine; uena, undecenylamine; ola, oleylamine; lla, linoleylamine. [b] Obtained for chloroform solutions 0.02–0.04 *M* in the complexes, at 298°K; error limits ±0.1 BM.

The adducts with the unsaturated amines other than allylamine were prepared in a similar manner, except that they were precipitated from dimethylformamide and recrystallized from ethyl acetate. These complexes are obtained as fine, somewhat sticky powders; otherwise, they are similar to the adducts with the saturated amines.

The complexes prepared are listed in Table I, along with melting points, analytical data, and magnetic moments. The analyses were obtained from Galbraith Laboratories.

Spectral and Magnetic Measurements.—Electronic spectra were taken on a Cary 14 recording spectrophotometer, Serial 244. Reflectance spectra in the visible and near-infrared regions were

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(1) For references prior to 1966, see the review article by J. P. Fackler, *Progr. Inorg. Chem.*, **7**, 361 (1966). For more recent work see, for example, P. E. Rakita, S. J. Kopperl, and J. P. Fackler, Jr., *J. Inorg. Nucl. Chem.*, **30**, 2139 (1968); M. K. Misra and D. V. Ramana Rao, *ibid.*, **31**, 3875 (1969); T. Shigematsu, T. Honjyo, M. Tabushi, and M. Matsui, *Bull. Chem. Soc. Jap.*, **43**, 793 (1970).

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measured with the total diffuse reflectance accessory for this instrument. Spectra were also taken of Nujol mulls painted onto filter paper. Solution spectra were measured in matched quartz cells of 0.1–2-cm path length.

Infrared spectra were recorded on a Perkin-Elmer 621 grating spectrophotometer, using Nujol mulls on CsBr plates.

The magnetic susceptibilities of some of the complexes were determined by nmr, using the method of Evans.[4] The solvent was chloroform; the inert reference material was tetramethylsilane (1% v/v). The solutions also contained 10% by volume of free amine, added to repress dissociation of the coordinated amine molecules. The same amount of amine was added to the solvent blank. A Wilmad precision coaxial cell was employed for the measurements. The measured susceptibilities were corrected for the diamagnetic susceptibilities of the ligand atoms, using the values listed by Figgis and Lewis.[5] The effective magnetic moments were then calculated from the equation $\mu_{\mathrm{eff}} = 2.84(\chi_{\mathrm{M}}'T)^{1/2}$, where χ_{M}' is the corrected molar susceptibility.

Solubility Measurements.—Saturated solutions of the complexes in the solvent of interest were prepared. The solutions were filtered or centrifuged, and the visible absorption spectra of the clear solutions were measured. Concentrations were checked by adding free amine (less than 5% by volume) to the solutions and rerunning the visible spectra; concentrations were then calculated from previously determined molar absorptivities.

Results and Discussion

Spectral and Magnetic Properties.—The cobalt compounds show almost identical reflectance spectra, as do the nickel compounds. The visible and near-infrared spectra are very similar to those reported by Hashagen and Fackler for their amine adducts.[2] The nickel compounds show weak bands at 9700 and 16,900 cm^{-1}, plus an intense ultraviolet band at 32,000 cm^{-1}. The cobalt compounds show a weak band at 9100 cm^{-1}; in the visible region, they show a plateau with shoulders at ~18,500, 19,800, and 21,300 cm^{-1}. An intense ultraviolet band occurs at 35,100 cm^{-1}.

Of the various solvents tried, only methylene chloride and chloroform gave solutions of the complexes concentrated enough for accurate measurements of solution spectra. In the absence of excess amine, solutions in these solvents showed colors and spectra indicating dissociation of amine molecules and polymerization of the metal acetylacetonates.[6,7] Upon addition of excess amine, the color of the cobalt solutions changed from orange-red to orange, that of the nickel solutions from blue-green to blue, and spectra close to the reflectance spectra were produced. The visible and near-infrared spectra of the nickel complexes are very similar to those previously reported for benzene solutions of amine adducts of Ni(acac)$_2$.[2] The intense ultraviolet band observed for the complexes is characteristic of octahedral bis adducts of the metal acetylacetonates.[8,9]

The infrared spectra of the parent acetylacetonates and of the bis-pyridine adduct of Ni(acac)$_2$ have been reported by Nakamoto, *et al.*, and the bands have been assigned.[10,11] The adducts prepared in the present investigation show the bands of the acetylacetonates plus additional bands, of which the most noteworthy are the following: (1) Bands ascribable to N–H stretching of the coordinated amines[12] are found at 3280 and 3190 cm^{-1}. (2) A series of weak bands is found in the region 1350–950 cm^{-1}. For the saturated amines, the number of bands increases with increasing chain length of the amine. Contributions from methylene wagging, NH$_2$ symmetric deformation, and various skeletal vibrations would be expected in this region, but overlap with acetylacetonate bands renders assignments difficult. The adducts with the unsaturated amines, which contain shorter methylene chains than the corresponding saturated amines, show fewer bands. (3) A band ascribable to vinyl CH$_2$ out-of-plane deformation[13] is found at 905 cm^{-1} in the spectra of the aa and uena adducts. (4) A band at 720 cm^{-1}, which increases in intensity with increasing chain length of the amine, can be assigned to a rocking mode of the methylene chains.[14] (5) The band lying between 550 and 600 cm^{-1} for the acac compounds and tentatively assigned to out-of-plane bending[10] is shifted to lower frequencies in the adducts.[14a] The cobalt compounds show a greater shift (25–30 cm^{-1}) than the nickel compounds (~10 cm^{-1}). The position of this band provides the only distinct difference between the infrared spectra of corresponding cobalt and nickel complexes.

The magnetic moments (Table I) are of the order usually obtained for octahedral complexes of cobalt(II) and nickel(II). No significant variation of moment with structure is evident.

All of the analytical, spectral, and magnetic data are in line with the formulation of the complexes as octahedral bis adducts of the amine molecules with the metal acetylacetonates. The bis-pyridine adducts of both cobalt(II) and nickel(II) acetylacetonates are known to be trans in structure,[2,15] although the bis(pyridine) *N*-oxide adduct of Ni(acac)$_2$ has been shown to be cis.[16] Hashagen and Fackler[2] assumed trans coordination of their *n*-propylamine and *n*-butylamine adducts on the basis of similarity of electronic spectra to the spectra of the pyridine adducts. In the case of the adducts reported here, the lengths of the hydrocarbon chains of the amines would, from packing considerations, render cis coordination in the solid state highly unlikely.

Solubilities.—One of the more interesting properties of the adducts is their solubility. At room temperature, the adducts are insoluble in water and only sparingly soluble in most organic solvents. They are soluble in dichloromethane and chloroform. In noncoordinating solvents such as benzene, carbon tetrachloride, and trichloroethylene they show a variation in solubility with structure. ("Solubility" as used here refers to molar solubility.) The solubilities of the adducts in carbon tetrachloride are shown in Table II. It is seen that the solubility is influenced by three factors: (1) The metal atom. In all cases, the cobalt complexes are more soluble than the corresponding

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TABLE II
MOLAR SOLUBILITIES OF $M(acac)_2(am)_2$ COMPOUNDS IN CCl_4

	Soly × 10^2			Soly × 10^2	
Adduct	Ni compd[a]	Co compd	Adduct	Ni compd[a]	Co compd
nha	0.75	1.9	hda	Insol	<0.3
noa	0.78	2.2	aa	0.28	1.8
nua	1.2	5.8	uena	4.8	19
trda	0.67	1.7	ola	8.9	24
ttda	<0.2	1.1	lla	9.1	24

[a] Solubilities calculated from visible absorption spectra of saturated solutions.

nickel complexes. (2) The length of the amine hydrocarbon chain. The *n*-alkylamine adducts show an increase in solubility with increasing chain length, followed by a sharp decrease. Of the complexes of *n*-alkylamines prepared, the undecylamine adduct is the most soluble and the hexadecylamine adduct the least soluble. (3) Unsaturation in the amine hydrocarbon chain. The presence of double bonds in the long chains greatly increases the solubility of the adducts. The uena adducts are several times as soluble as the nua adducts, and the ola and lla adducts are still more soluble.

Recently, Rapp and Pavkovic[17] reported the preparation of complexes of the type $[Ni(am)_6](ClO_4)_2$, where am is a long-chained primary amine. They found that the chain length of the amine had no influence upon ease of complex formation. In this work, chain length was found to have no influence upon ease of adduct formation; of the properties measured, the only ones affected by chain length are melting point and solubility.

Acknowledgments.—The author is most grateful to Dr. R. A. Henry for preparation of the undecenylamine, to Mr. D. W. Moore for the magnetic susceptibility measurements, and to Dr. A. Adicoff for helpful discussion.

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Preparation and Coordination Chemistry of 1,4-Cyclooctadiene

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Very little attention has been paid to the reactions of 1,4-cyclooctadiene (1,4-COD) with transition metal ions, in comparison with the extensively investigated 1,5-COD and 1,3-COD.[1] This is due to the fact that the known methods of preparation of 1,4-COD are either tedious[2] or involve rather expensive starting materials.[3]

1,4-COD has been encountered as a reaction intermediate in the homogeneous catalytic isomerization of 1,5-COD to 1,3-COD[4] and in the rearrangement of coordinated 1,3-COD to 1,5-COD in Pd(II) complexes.[5] Information on the coordination chemistry of 1,4-COD may, therefore, throw some light on the mechanisms of these isomerization and rearrangement reactions.

The present work has been undertaken to find a convenient method for the preparation of 1,4-COD, and to investigate reactions of 1,4-COD with some transition metal ions.

Experimental Section

Materials.—*cis*-$Pt\{(C_6H_5)_3P\}_2Cl_2$[6,7] and $Pd(C_6H_5CN)_2Cl_2$[8] were prepared by methods reported in the literature. 1,5-COD was distilled under reduced pressure before use. Its purity was checked by gas chromatography.

1,4-COD was prepared by the controlled isomerization of 1,5-COD. Two grams of $Pt\{(C_6H_5)_3P\}_2Cl_2$ and 5.0 g of $SnCl_2 \cdot 2H_2O$ were dissolved in 150 ml of CH_2Cl_2. 1,5-COD (300 ml) was added and the reaction mixture was stirred in a Parr high-pressure reactor under 600 psi of hydrogen at 75° for 4 hr. The recovered COD mixture (275 ml) consisted of 36% 1,5-COD, 42% 1,4-COD, and 22% 1,3-COD. 1,5-COD was separated from the diene mixture by an efficient fractionating column. 1,4-COD was separated from the mixture of 1,3-COD and 1,4-COD by the method of $AgNO_3$ adduct formation.[2] Seventy-five milliliters of pure (>99.5% by VPC) 1,4-COD was obtained; bp 114.2° (758 mm); $n^{23}{}_D$ 1.4894; ir (neat): 1645 (C=C); nmr (CCl_4) consisted of four multiplets due to 4, 2, 4, and 2 H's, respectively, centered at τ values of 4.48 (–(H)C=C(H)–), 7.23 (=CC(H_2)C=), 7.72 (=CC(H_2)C–), and 8.60 ppm (=CCC(H_2)CC=).

Reactions of 1,4-COD with Some Transition Metal Ions.—Some of the properties of the products of the reaction of 1,4-COD with some transition metal ions are shown in Table I.

$RhCl_4 \cdot 3H_2O$.—To a solution of 0.50 g of $RhCl_3 \cdot 3H_2O$ in 10 ml of absolute ethanol 1 ml of 1,4-COD was added and the mixture was stirred for 2.5 hr at 60°. A complex identical with [Rh(1,5-COD)Cl]$_2$[9] was obtained.

Attempts to prepare a complex of Rh(I) in which 1,4-COD is unrearranged, by running the reaction at 3–4° for 2 days, have failed.

$IrCl_3 \cdot 3H_2O$.—The reaction was carried out in a manner similar to that of $RhCl_3 \cdot 3H_2O$ for 12 hr. A complex identical with [Ir(1,5-COD)HCl_2]$_2$[10] was obtained.

$Pd(C_6H_5CN)_2Cl_2$.—To a solution of 0.50 g of $Pd(C_6H_5CN)_2Cl_2$ in 10 ml of benzene was added 1 ml of 1,4-COD. The yellow precipitate obtained was filtered and washed with benzene and petroleum ether (bp 30–75°), respectively. *Anal.* Calcd for $C_8H_{12}Cl_2Pd$: C, 33.81; H, 4.25; Cl, 24.61. Found: C, 33.90; H, 4.32; Cl, 24.48.

When a suspension of 1.00 g of $Pd(C_6H_5CN)_2Cl_2$ in several milliliters of 1,4-COD was stirred for 1.5 hr, a yellow precipitate separated; mp 185–198 dec. Decomposition of the product with aqueous KCN gave a mixture of 1,4-COD and 1,5-COD.

K_2PtCl_4.—A solution of 0.50 g of K_2PtCl_4 in 30 ml of 50% ethanol containing 1 ml of 1,4-COD was stirred overnight. The white compound obtained was recrystallized from acetic acid. Although analysis for the olefin shows it to be Pt(1,5-COD)Cl_2, the complex is different from that obtained by the reaction of K_2PtCl_4 with 1,5-COD under similar conditions.

CuCl.—The reaction of 1,4-COD with CuCl in aqueous HCl or with $CuCl_2 \cdot 2H_2O$ in ethanol in the presence of a reducing agent gave [Cu(1,4-COD)Cl]$_2$. *Anal.* Calcd for $C_8H_{12}ClCu$: Cu, 30.7. Found: Cu, 30.2.

$AgNO_3$.—Reaction of 1 ml of 1,4-COD with 3 ml of 50% aqueous $AgNO_3$ solution gave [Ag_2(1,4-COD)](NO_3)$_2$. *Anal.* Calcd for $C_8H_{12}N_2O_6Ag_2$: Ag, 48.2. Found: Ag, 48.3. Equivalent conductance of a 0.01 *M* aqueous solution is 5.1 ohm^{-1} cm^2 corresponding to a 1:2 electrolyte.

$HAuCl_4$.—An unstable, light-sensitive compound was obtained

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