TABLE II

NORMAL-COORDINATE ANALYSIS RESULTS FOR $Ir_4(CO)_{12}$

Raman freq, cm^{-1}		
Obsd	Calcd	ν_{M-M}[a]
207	206.9 (A_1)	90.8
161	161.2 (T_2)	88.2
131	130.9 (E)	83.5
102	99.6 (T_2)	1.5
94	96.5 (E)	5.4
85	79.7 (T_2)	6.0
72	76.4 (A_1)	5.6
40	40.8 (T_2)	0.9
40	39.0 (E)	7.0

$K_{M-M} = 1.69$ mdyn/Å $K_{M-M-C} = 0.12$ mydn-Å
k'_{M-M}[b] $= -0.13$ mydn/Å $K_{C-M-C} = 0.19$ mdyn-Å
k''_{M-M}[b] $= 0.13$ mdyn/Å k'_{C-M-C}[b] $= 0.10$ mdyn-Å

[a] Percentage contribution to the potential energy from the metal–metal coordinate. [b] Interaction constants: k'_{M-M}, between adjacent metal–metal bonds; k''_{M-M}, between opposite metal–metal bonds; k'_{C-M-C}, between adjacent C–M–C angles.

cluster frequencies requires, in addition to the primary metal–metal stretching constant, both interaction constants (for adjacent and nonadjacent bonds).

Table II lists the adjusted force constants, compares observed and calculated frequencies, and gives the contribution of the metal–metal coordinate to the potential energy of each of the low-frequency normal modes. Mixing of cluster modes with M–C deformation modes is quite limited, less than was observed for $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$.[2] On the other hand, with the reassignment of the E cluster mode, the cluster frequency ratios, $\nu_{A_1}:\nu_{T_2}:\nu_E = 2:1.56:1.27$, are further from the simple cluster prediction than was thought,[3] reflecting the requirement for substantial metal–metal interaction constants. It is evident that simple cluster predictions must be treated with some caution in making band assignments.

The value of the primary metal–metal force constant is much higher for $Ir_4(CO)_{12}$ (1.69 mdyn/Å) than for $Os_3(CO)_{12}$[2] (0.91 mdyn/Å). While the direction of the difference is consistent with the increase in metal–metal distance (2.68 Å for $Ir_4(CO)_{12}$,[4] 2.89 Å for $Os_3(CO)_{12}$[8]), its size is disproportionate and no doubt reflects the greater complexity of the $Ir_4(CO)_{12}$ force field. Indeed the symmetry force constants for the A_1 breathing modes, 1.30 and 0.91 mdyn/Å, respectively, for $Ir_4(CO)_{12}$ and $Os_3(CO)_{12}$, seem to provide a more reasonable basis for comparison. The force constants for metal–carbon deformation are substantially lower for $Ir_4(CO)_{12}$ than for $Os_3(CO)_{12}$, although they are not directly comparable in view of the different forms of the redundancies in the two calculations.

Experimental Section

$Ir_4(CO)_{12}$ was obtained from Alfa Inorganics, Inc., and was purified by sublimation in a stream of CO. Infrared spectra were recorded on a Beckman IR12 spectrometer using Nujol mulls. Raman spectra were obtained with microcrystalline samples using a spectrometer[9] equipped with an He–Ne laser source. The instrument was calibrated using helium and argon discharge lines. Attempts to grow single crystals of sufficient size and quality for polarization studies were unsuccessful.

Acknowledgments.—We are indebted to Drs. L. F. Dahl and E. W. Abel for communicating results of their work in advance of publication.

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Nickel(II) Complexes of Some Tetradentate Salicylaldimine Ligands[1]

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The relationships between spectral and magnetic properties and stereochemistry of four-coordinate Ni(II) and Co(II) complexes of salicylaldimine ligands are well established.[2] Monomeric bis complexes occur in either the planar (low-spin) or the pseudotetrahedral (high-spin) configuration in the solid state. In solutions of noncoordinating solvents some Ni(II) complexes become involved in a rapid equilibrium between the two limiting configurations. Presumably the planar → tetrahedral configurational change involves a rotation of the two chelate ring planes with respect to one another such that the dihedral angle between them changes from ~0° (planar) to ~90° (tetrahedral). This is accompanied by a change in spin state.

We are interested in designing ligands which force an intermediate stereochemistry on four-coordinate complexes of Ni(II) and Co(II) in hopes of obtaining some complexes at the point of spin-multiplicity change. It appeared that tetradentate complexes of I offer a reasonable chance of success for M = Ni(II). Cu(II) complexes of structure I become increasingly distorted from planarity as n is increased.[3] The Co(II) complexes of I where $n = 4$–10 are tetrahedral,[4] the $n = 3$ complex is high spin and is believed to have a flattened tetrahedral structure,[4b] and the $n = 2$ complex is planar.[5] Ni(II) complexes of Schiff bases derived from pyrrole-2-carboxaldehyde and diamines having two to five carbons are diamagnetic and monomeric.[6] Ni(II) complexes of structure I with $n = 2$–4 are diamagnetic and presumably planar or nearly planar.[7] This note

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(1) This research was supported by the National Science Foundation under Grant GP-8871.

(2) See R. H. Holm, G. W. Everett, Jr., and A. Charkravorty, *Progr. Inorg. Chem.*, **7**, 83 (1966), for an extensive list of references.

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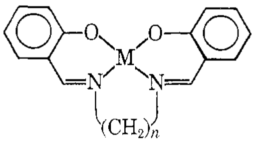
presents the results of an investigation of the higher homologs of this series of Ni(II) complexes for which the *simplest* formulation is I, where $n = 5$–12.



I

Experimental Section

Synthesis of Ligands.—The polymethylenediamines were allowed to reflux with a slight excess of salicylaldehyde in absolute ethanol. The resulting yellow solids were recrystallized several times from ethanol and characterized by their pmr spectra.

Preparation of Complexes.—The Ni(II) complexes were prepared by allowing purified ligand to react with nickel acetate in absolute ethanol. The reaction mixtures were refluxed several hours; then the products were collected on a filter and washed several times with hot ethanol. The solvent was removed *in vacuo*.

Magnetic Susceptibility Measurements.—All magnetic susceptibility measurements were performed on crystalline samples. Room-temperature measurements were made by the Gouy method using aqueous nickel chloride as the standard. Measurements at −78° were carried out on a Faraday apparatus using $HgCo(CNS)_4$ as the standard. Cooling was achieved by immersing the evacuated sample chamber in a freshly prepared CO_2–C_7H_{16} mixture during the experiment. In all cases several readings were made at each of several field strengths. At least two tube packings were made for each sample measured by the Gouy method. Magnetic moments were calculated from the Curie law.

Spectral Measurements.—Electronic absorption spectra of complexes in mineral oil mulls were recorded in the visible and near-infrared regions using a Cary Model 14 spectrophotometer. Infrared spectra in the 2.5–15-μ region were measured on a Perkin-Elmer Model 421 spectrophotometer. The complexes were mulled in Nujol.

X-Ray Powder Patterns.—X-Ray powder patterns were made with a Debye–Scherrer powder camera of 57.3-mm radius using Cu Kα radiation with a Ni filter. An exposure time of 8 hr was used in each case.

Results

The N,N′-polymethylenebis(salicylideniminato)-nickel(II) complexes (I, $n = 5$–12) were found to have very low solubilities in most solvents except pyridine, a coordinating solvent, and all physical measurements had to be carried out on the solid phase. Elemental microanalyses demonstrated the purity of each sample used in physical studies.[8] Ligand field spectral and magnetic data are given in Table I. The complex having $n = 5$ is diamagnetic as are the lower members of the series,[7] but for complexes having $n = 6$–12 various effective moments are observed. Diamagnetic samples are obtained for the $n = 11$ and 12 complexes if excess ligand is used in the reaction mixture, but use of stoichiometric amounts of ligand leads to paramagnetic products. Effective moments range from 1.65 to 3.08 BM over several preparations for the $n = 12$ complex. Both diamagnetic and paramagnetic samples have the same elemental composition.

TABLE I

MAGNETIC AND LIGAND FIELD SPECTRAL DATA[a]

n	μ_{eff}, BM	λ_{max},[c] cm^{-1}	
5	Diamagnetic	16,000	
6	~1.1[b]	16,100	
7	~1.2[b]	16,200	
8	~1.6[b]	15,900	10,000–9100
9	2.82	16,000	9,360
10	1.82	16,000	10,000–8400
11	2.46	16,000	9,400
11	Diamagnetic	16,220	
12	1.65–3.08	16,000	9,400
12	Diamagnetic	16,300	

[a] All measurements were made on solid samples at normal room temperature (20–25°). [b] Errors of the order of ±0.1 BM may be present owing to the small magnitude of observed sample deflections. [c] Data from mineral oil mulls.

Mull spectra of the diamagnetic complexes show a single ligand field band in the visible region around 16000 cm^{-1}. An absorption in this region also occurs for the paramagnetic complexes, but, in addition, a band appears in the near-infrared region around 9400 cm^{-1} for complexes having moments greater than ~1.5 BM (see Table I and Figure 1). The intensity and resolution of this latter band roughly parallel the observed magnetic moments.

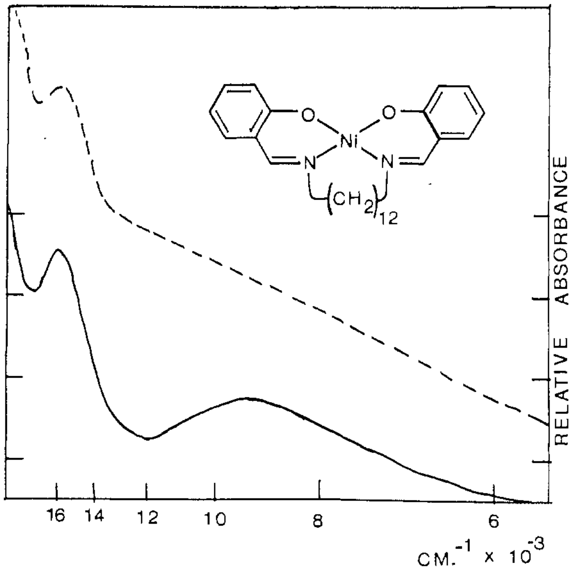


Figure 1.—Electronic absorption spectra of N,N′-dodecamethylenebis(salicylideniminato)nickel(II) in mineral oil mulls: – – – –, diamagnetic sample; ———, sample with $\mu_{eff} = 2.80$ BM.

Discussion

The electronic absorption spectra of the more strongly paramagnetic complexes ($n = 8$–12) indicate the nickel ions are octahedrally coordinated. The mull spectrum of the paramagnetic form of the $n = 12$ complex (Figure 1) is typical. The absorption around 9400 cm^{-1} is well defined for complexes having moments greater than 2 BM ($n = 9$, 11, 12) and is weak but discernible for complexes which have lower moments ($n = 8$, 10). This absorption occurs in solid-state and solution spec-

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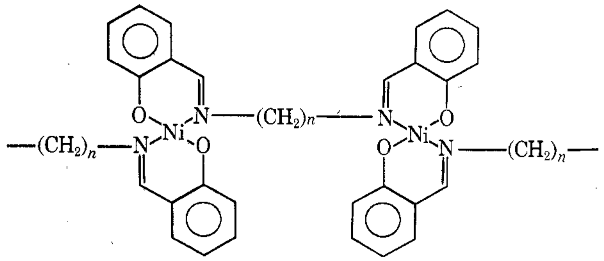
(8) Values found for C, H, and N were all within ±0.4, ±0.3, and ±0.2%, respectively, of the theoretical values except for the $n = 9$ complex. The latter could not be obtained in high purity. *Anal.* Calcd: C, 65.28; H, 6.67; N, 6.62. Found: C, 64.73; H, 6.70; N, 6.05.

tra of bis(N-*m*-substituted arylsalicylaldiminato)nickel(II) complexes known to be extensively associated.[9] It is also found for complexes such as bis(N-R-salicylaldiminato)nickel(II), where R = $CH(CH_3)CH_2OCH_3$, which attains an octahedral ligand field through intramolecular coordination of the oxygens on the R groups.[10] The absorption at ~16,000 cm^{-1} is found in the mull spectra of all complexes where $n = 5$–12. However, an absorption has been observed in this region not only for the diamagnetic complexes I where $n =$ 3, 4[7] but also for the associated bis(N-arylsalicylaldiminato)nickel(II) complexes[9] and the monomeric octahedral complex mentioned above where R = $CH(CH_3)$-CH_2OCH_3.[10] No absorption could be detected in the 6800-cm^{-1} region where tetrahedral salicylaldimine complexes of Ni(II) characteristically absorb. Furthermore, the spectra of complexes I in the near-infrared region are quite unlike those reported for five-coordinate nickel(II) complexes of the salicylaldimine series.[11]

The spectral observations outlined above strongly imply that octahedrally coordinated nickel ions are present in the solid state of complexes I where $n = 6$–12 and are responsible for the observed paramagnetism. However, most of the observed moments are considerably lower than the ~3.2 BM expected for octahedral nickel(II). Infrared spectra of diamagnetic and strongly paramagnetic samples of the $n = 12$ complex are quite similar and show no absorption which can be attributed to coordinated water. Also the elemental microanalyses give no indication of the presence of water. Paramagnetic impurities such as nickel acetate or nickel hydroxide would be detected by elemental analyses unless they are present to the extent of only ~3 mol % or less. In this case their maximum contribution to μ_{eff} would be ~0.6 BM, and their contribution to the absorption spectra would be negligible. It appears that the existence of a singlet–triplet equilibrium arising from a tetragonal ligand field[12] is not responsible for the anomalous moments, at least for the $n = 11$ and 12 complexes. Moments of these complexes are unchanged (within 0.05 BM) upon going from 293 to 195°K.[13]

We find the above results consistent with the presence of magnetically nonequivalent nickel ions in the solid samples: a fraction of the ions are octahedrally coordinated and high spin as a result of molecular association, whereas the others are planar and low spin. In order to determine if mixed crystals occur in samples having anomalous moments, X-ray powder patterns were made of three samples of the $n = 12$ complex. The samples chosen had moments of 0, 2.00, and 3.03 BM. It was expected that distinctly different patterns would be found for the samples having $\mu_{eff} = 0$ and 3.03 BM and that the pattern for the sample with $\mu_{eff} =$ 2.00 BM would contain lines present in both of the other patterns. However, all three patterns contained common features, and resolution of the lines decreased markedly with increasing μ_{eff}. These data do not unambiguously demonstrate the occurrence of mixed crystals in the 2.00-BM sample, since it is not clear whether the high-spin form lacks crystallinity or is incapable of giving a good powder pattern for other reasons.

Some discussion of the mode of chelation is in order, especially for those ligands where the salicylaldimine groups are separated by a long hydrocarbon chain. In *addition* to a tendency to form molecular aggregates through sharing of donor oxygens, it is also quite possible that the complexes become polymeric through sharing of ligands. A possible structure is II, where the principal coordination is *trans* planar. Unfortunately, the low solubility of the complexes precludes molecular weight measurements. Space-filling molecular models indicate, where $n = 8$–12, strained *trans*-planar and *cis*-planar monomers are possible, but an unstrained model of II is easily made. Furthermore, there is little steric inhibition to association by means of which a number of polymeric chains such as II could be joined laterally by sharing donor oxygens. Thus, we believe the most plausible structure for the higher homologs, at least, of the N,N′-polymethylenebis(salicylideniminato)nickel(II) complexes is II. In paramagnetic samples some of oxygens are shared, forming octahedrally coordinated nickel and joining the polymeric chains.



II

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(13) Samples having intermediate moments (2.46 BM for $n = 11$ and 2.64 BM for $n = 12$) were chosen for this experiment.

A New β-Diketonate Complex of Silicon(IV)

BY DAVID W. THOMPSON

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Recently there has been much interest in dichlorobis(acetylacetonato) complexes of the group IV elements