$(NCH_3)_3$ increases with decreasing R value, going from a limpid liquid at $R = 3$ to an extremely viscous, nearly solid, homogeneous, transparent mass at $R = 0.23$. This means that the neat liquids flow at R values below the "gel point" calculated from fitting the proton n.m.r. data of Table II to the statistical theory of ring-free molecules at equilibrium with respect to exchange of their parts. Of course, the presence of ring structures, including cages based on fused rings, can shift the "gel point" in the extreme case to $R = 0$. However, it is expected that the presence of a moderately large fraction of the total As in ring structures at $R = 1.12$ would lead to amounts at higher R values sufficiently large so as to spoil the fit between experiment and theory in Table II. An alternative explanation for flow beyond the "gel point" corresponding to no rings in the finite molecules would be a sufficiently rapid making and breaking of As–N bonds in the network structure to permit flow by this mechanism. Presumably the "gel point" appears at a somewhat lower R value than presented above for a ring-free system and the observed flow is due in part to the making and breaking of chemical bonds holding the parts of the molecules together.

Conclusions

As was found in the case of the polyarsenous oxyfluorides[10]— which form a family of compounds similar to the one described herein except that the arsenic atoms are linked together in the molecules by oxygens rather than methylimino bridges, the poly(fluoroarsenous methylimides) consist of labile molecules which exchange parts with each other so rapidly at room temperature that they would be impossible to separate by standard methods. However, unlike the AsF_3–As_2O_3 system,[10] which corresponds to nearly

random sorting, the end and middle groups are present in much greater amounts than randomly expected in the system AsF_3–$As_2(NCH_3)_3$. This means that an appreciable energy is associated with the exchange of methylimino bridges for fluorine atoms on an arsenic, and this may be explained in terms of nonbonding interactions arising from electron correlation.[11] Such nonrandom behavior is in accord with our findings on exchange of dimethylamino groups with halogens in *neso* compounds based on a single arsenic,[2] phosphorus,[12] germanium,[13] or silicon atom.[14]

When the values of the equilibrium constants relating structure-building units are considerably smaller than their random values, as in the case of the family of compounds studied here ($K_1 = 0.10$ and $K_2 = 0.05$ as compared to $K_{rand} = 0.33$), straight-chain oligomers are produced when the ring-chain equilibria are shifted toward the chains, as has been found to be true in this case. Thus, for $R = 1.125$, we calculate that 70% of the molecules and 20% of the total arsenic are present in unbranched-chain molecules, with 5% of the total arsenic in straight chains having 10 or more arsenic atoms in their structure. This paper exemplifies the fact that the study of deviations from random sorting of substituents in scrambling reactions of simple compounds may be employed to predict the structural properties of a previously unknown family of compounds of sufficient lability so that the preparative operations lead to full or partial equilibration with respect to exchange of parts between the molecules. A general theoretical treatment of such systems is underway in our laboratory.

(11) D. E. Petersen and K. S. Pitzer, *J. Phys. Chem.*, **61**, 1252 (1957); K. S. Pitzer and E. Catalano, *J. Am. Chem. Soc.*, **78**, 4565, 4844 (1956).

(12) J. R. Van Wazer and L. Maier, *ibid.*, **86**, 811 (1964).

(13) G. Burch and J. R. Van Wazer, results in preparation for publication.

(14) K. Moedritzer and J. R. Van Wazer, *Inorg. Chem.*, **3**, 268 (1964).

(10) J. R. Van Wazer, K. Moedritzer, and D. W. Matula, *J. Am. Chem. Soc.*, **86**, 807 (1963).

Investigation on the Occurrence of Tetrahedral Forms of Substituted Bis(N-alkylsalicylaldimino)nickel(II) Complexes[1]
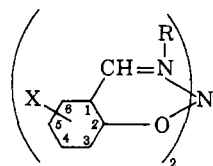
BY L. SACCONI, M. CIAMPOLINI, AND N. NARDI

Spectrophotometric, magnetic, osmotic, and dielectric polarization measurements on three series of ring-substituted R-N-salicylaldimino-nickel(II) complexes (R = *n*-propyl, *sec*-alkyl, *t*-butyl) have been made. In the solid state the *n*-propyl derivatives are planar, the *t*-butyl derivatives pseudo-tetrahedral. The *sec*-alkyl complexes are either planar or pseudo-tetrahedral depending on the nature and position of the ring substituent. In inert solvents at room temperature the *n*-propyl derivatives are essentially planar, the *t*-butyl derivatives largely pseudo-tetrahedral; the *sec*-alkyl complexes generally exist in comparable proportions of either forms. The proportion of the tetrahedral form in the *n*- and isopropyl complexes increases with increasing temperature; the opposite occurs in the *t*-butyl derivatives. The enthalpy and entropy changes were calculated from the temperature dependence of the constant for the equilibrium between planar and tetrahedral allogons. The results are discussed in terms of electronic factors and steric requirements of the ligand groups.

Introduction

We have recently shown that the paramagnetism of many N-*sec*-alkyl,[2] N-*n*-alkyl,[3] and N-arylsalicylaldiminonickel(II)[4] complexes is often due to a tetrahedral structure, both in the solid state and in solution; an X-ray structural investigation then showed unambiguously that the isopropyl derivative has the tetra-

(1) This research was supported by the U. S. Department of the Army through its European Research Office, under Contract No. DA-91-591-EUC-2965, and by the Italian "Consiglio Nazionale delle Ricerche."

(2) L. Sacconi, P. L. Orioli, P. Paoletti, and M. Ciampolini, *Proc. Chem. Soc.*, 255 (1962); L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Am. Chem. Soc.*, **85**, 411 (1963); later these results were confirmed by R. H. Holm and K. Swaminathan, *Inorg. Chem.*, **2**, 181 (1963).

(3) L. Sacconi, *J. Chem. Soc.*, 4608 (1963).

(4) L. Sacconi and M. Ciampolini, *J. Am. Chem. Soc.*, **85**, 1750 (1963).

hedral configuration.[5] With the aim of studying the factors which influence the occurrence of such a structure we prepared some series of nickel(II) complexes with ring-substituted N-alkylsalicylaldimines of the general formula

(5) M. R. Fox, E. C. Lingafelter, P. L. Orioli, and L. Sacconi, *Nature*, **197**, 1104 (1963).

TABLE I

SUMMARY OF PHYSICAL AND ANALYTICAL DATA OF SUBSTITUTED BIS(R-N-SALICYLALDIMINO)NICKEL(II) COMPLEXES

R	X	Crystallization or purification	M.p., °C.	Formula	—% calcd.—		—% found—		—Mol. wt.—	
					N	Ni	N	Ni	Calcd.	Found
n-Propyl	H	CHCl₃ + EtOH	160–161	$C_{20}H_{24}N_2O_2Ni$	7.32	15.33	7.55	15.22	383	379[a]
	3-Me	Cyclohex.	144–146	$C_{22}H_{28}N_2O_2Ni$	6.81	14.27	7.06	14.25	411	414
	3-Cl	C₆H₆ + cyclohex.	137–138	$C_{20}H_{22}Cl_2N_2O_2Ni$	6.20	12.98	6.08	13.11	452	454
	5-Me	C₆H₆ + cyclohex.	123–124	$C_{22}H_{28}N_2O_2Ni$	6.81	14.27	6.96	14.32		
	5-Cl	C₆H₆ + cyclohex.	214–215	$C_{20}H_{22}Cl_2N_2O_2Ni$	6.20	12.98	6.25	12.95	452	457
	5-NO₂	Cyclohex.		$C_{20}H_{22}N_4O_6Ni$	11.84	12.40	11.87	12.33		
	3,4-Benzo	C₆H₆	177–178	$C_{28}H_{28}N_2O_2Ni$	5.80	12.14	6.03	12.26		
	5,6-Benzo	C₆H₆	204–206	$C_{28}H_{28}N_2O_2Ni$	5.80	12.14	5.84	12.18	483	485
Isopropyl	H	Cyclohex.	205–207	$C_{20}H_{24}N_2O_2Ni$	7.32	15.33	7.53	15.58	383	439[a]
	3-Me[b]	CHCl₃ + petr. ether	130–131	$C_{22}H_{28}N_2O_2Ni$	6.81	14.27	6.96	14.16		
	3-Cl	Cyclohex.	168–169	$C_{20}H_{22}Cl_2N_2O_2Ni$	6.20	12.98	6.27	12.93	452	452
	5-Me	CHCl₃ + petr. ether	153–154	$C_{22}H_{28}N_2O_2Ni$	6.81	14.27	6.83	14.17	411	431
	5-Cl	Cyclohex.	195–196	$C_{20}H_{22}Cl_2N_2O_2Ni$	6.20	12.98	6.41	12.95	452	449
	5-NO₂	CHCl₃		$C_{20}H_{22}N_4O_6Ni$	11.84	12.40	11.99	12.51		
	3,4-Benzo	CHCl₃ + cyclohex.	227–229	$C_{28}H_{28}N_2O_2Ni$	5.80	12.14	5.73	12.18	483	488
	5,6-Benzo	CHCl₃ + cyclohex.	208–209	$C_{28}H_{28}N_2O_2Ni$	5.80	12.14	5.84	12.03	483	473
sec-Butyl	5,6-Benzo	Cyclohex.	144–145	$C_{30}H_{32}N_2O_2Ni$	5.48	11.48	5.47	11.47		
t-Butyl	H	Sublimed 180° (10⁻⁴ mm.)	202–203	$C_{22}H_{28}N_2O_2Ni$	6.82	14.27	6.80	14.12	411	431[a]
	3-Cl	Sublimed 180° (10⁻⁴ mm.)	284–286	$C_{22}H_{26}Cl_2N_2O_2Ni$	5.84	12.22	5.82	12.08	480	463
	5-Cl	Sublimed 180° (10⁻⁴ mm.)	234–236	$C_{22}H_{26}Cl_2N_2O_2Ni$	5.84	12.22	5.95	12.29	480	433
	5-NO₂	C₆H₆		$C_{22}H_{26}N_4O_6Ni$	11.17	11.71	11.29	11.77		
	3,4-Benzo	C₆H₆	>240	$C_{30}H_{32}N_2O_2Ni$	5.48	11.48	5.02	11.52		
	5,6-Benzo	C₆H₆	254–256	$C_{30}H_{32}N_2O_2Ni$	5.48	11.48	5.53	11.55	511	476

[a] Cf. ref. 2. [b] R. H. Holm and K. Swaminathan, *Inorg. Chem.*, **2**, 182 (1963).

in which X = 3-methyl, 5-methyl, 3-chloro, 5-chloro, 5-nitro, 3,4-benzo, and 5,6-benzo, and R consisted of three types of alkyl groups with increasing branching at the α-carbon atom, n-propyl, isopropyl and sec-butyl, and t-butyl.

Having found that the band at *ca.* 6700 cm.⁻¹ is diagnostic of the tetrahedral structure in these chelates,[2,3] we used the spectra to determine both the structure of the complexes and the constants for the planar ⇌ tetrahedral allogonal equilibria which exist in inert solvents such as benzene, *m*-xylene, and bibenzyl. The enthalpy and entropy differences between the isomers were calculated from measurements of the temperature coefficients of log *K*. Where necessary, the electric and magnetic moments and the molecular complexity were measured.

Experimental

Preparations of the Compounds.—The substituted bis(N-alkyl-salicylaldimino)nickel(II) compounds were prepared according to the procedure already described for the unsubstituted compounds.[2] The n-propyl, isopropyl, and sec-butyl derivatives were purified by recrystallization; the t-butyl derivatives were generally purified by sublimation at 170–180° (10⁻⁴ mm.) in order to prevent hydrolysis. Analytical and physical data of these compounds are summarized in Table I.

Spectrophotometric Measurements.—The absorption spectra were recorded with a Beckman DK2 spectrophotometer equipped with a thermostated cell housing of local design. Temperatures from 80 to 170° were obtained by circulating paraffin oil from a thermostat regulated to ±0.5°. Stoppered silica cells of 1 cm. path length were used. In calculating extinction coefficients, allowance was made for the variation of the density of the solution with the temperature. Bibenzyl was purified by repeated crystallization from light petroleum.

The reflectance spectra were measured using the standard Beckman reflectance attachment and magnesium oxide as the reference.

Magnetic Measurements.—The apparatus used for the magnetic measurements and the experimental technique were described in a previous paper.[6] The Gouy tube was calibrated using freshly distilled water, the specific susceptibility of which was assumed to be −0.720.10⁻⁶ at 20°. Diamagnetic corrections were calculated from Pascal's constants.[7]

Dielectric Polarization Measurements.—The apparatus and procedure used for the measurements of the dielectric constants and densities of the solutions already have been described.[8] The molar refractions for the sodium D line of the ring-substituted complexes of cobalt(II) and nickel(II) were calculated by adding the proper values of bond refractions[9] to the measured molar refractions of the nonsubstituted complexes.[2] Values of the orientation polarization, P_0, were calculated by assuming a value of 20% R_D for the atom polarization.[2]

Molecular Weight Determination.—Molecular weights were measured at 37° on benzene solutions using a Mechrolab osmometer. Benzene was distilled over phosphorus pentoxide through a Todd column packed with glass helices. The instrument was calibrated with benzil. The measurements on the substituted bis(N-t-butylsalicylaldimino)nickel(II) complexes were prevented by the slow hydrolysis of the compounds. The osmotic measurements for the substituted bis(N-t-butylsalicyl-aldimino)nickel(II) were not reproducible, probably on account of some decomposition of the compounds.

Results and Discussion

Stereochemistry of the Complexes in the Solid State.—Our previous studies of some chelate complexes of nickel(II) with N-alkyl[2,3] and N-arylsalicylaldimines[4] showed that those which have a pseudo-tetrahedral structure, are brown, and have absorption bands at 6700, 9500, 10,900, 14,100, 16,900, and 19,600 cm.⁻¹ in the region characteristic of crystal field transitions. On the other hand those with a planar structure are olive-green and have only one band at 16,000 cm.⁻¹ in the same region. These findings were used to interpret the reflectance spectra of the present compounds in the solid state. The conclusions are collected in Table II. This shows that in the solid state all the n-propyl derivatives are planar while all the t-butyl compounds are pseudo-tetrahedral. The isopropyl complexes are planar except for those with unsubstituted salicylaldehyde and with the 3,4-benzo derivative, which are pseudo-tetrahedral.

These structural assignments are confirmed by magnetic measurements. The magnetic moments (Table III) were zero for those complexes given the planar structure on spectroscopic grounds and 3.2–3.3 B.M.

(6) L. Sacconi, R. Cini, M. Ciampolini, and F. Maggio, *J. Am. Chem. Soc.*, **82**, 3487 (1960).

(7) P. W. Selwood, "Magnetochemistry," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1956.

(8) L. Sacconi, M. Ciampolini, F. Maggio, and F. P. Cavasino, *J. Inorg. Nucl. Chem.*, **19**, 73 (1961).

(9) A. I. Vogel, W. T. Cresswell, G. H. Jeffrey, and J. Leicester, *J. Chem. Soc.*, 514 (1952).

Table II

Structure of the X-Substituted Bis(R-N-Salicylaldimino)- nickel(II) Complexes in the Solid State from the Reflectance Spectra

							5,6-	3,4-
R	H	3-Me	5-Me	3-Cl	5-Cl	5-NO₂	Benzo	Benzo
n-Propyl	P[a]	P	P	P	P	P	P	P
Isopropyl	T	P	P	P	P	P	P	T
t-Butyl	T			T	T	T	T	T

[a] P = planar form, T = tetrahedral form; $\bar{\nu}_{max}$ (cm.$^{-1}$) of the planar form: 16,000 cm.$^{-1}$; $\bar{\nu}_{max}$ (cm.$^{-1}$) of the tetrahedral form: 6700, 9500, 10,900, 14,000, 16,900, and 19,600 cm.$^{-1}$.

Table III

Magnetic Susceptibility Data for Substituted Bis(R-N-salicylaldimino)nickel(II) Complexes

R	X	T, °C.	Solvent	$10^6 \times \chi_g$	$10^6 \times \chi_M$	μ_{eff} (B.M.)
n-Propyl	3-Cl	20		Diamagnetic		
	5-Cl	20		Diamagnetic		
	3,4-Benzo	21		Diamagnetic		
Isopropyl	3-Cl	19		Diamagnetic		
	5-Cl	22		Diamagnetic		
	5-Cl	24	C₆H₆	3.94	1975	2.17
	5-NO₂	20		Diamagnetic		
	3,4-Benzo	23		8.34	4356	3.22
	3,4-Benzo	21	C₆H₆	6.99	3674	2.95
	5,6-Benzo	24		Diamagnetic		
t-Butyl	3-Cl	17		9.19	4679	3.31
	5-Cl	30	C₆H₆	8.54	4368	3.27
	5,6-Benzo	24	C₆H₆	7.97	4416	3.25
	5,6-Benzo	24	C₆H₆	7.82	4339	3.22

Table IV

Dielectric Polarization Data for Some Substituted Bis-(R-N-Salicylaldimino)metal(II) Complexes in Benzene at 25°

M	R	X	$P_{2\infty}$	R_D	P_0	μ_D
Ni	n-Propyl	H[a]	140	117	0	0.00
		3-Cl	158	127	6	0.54
		5-Cl	169	127	16	0.91
		5,6-Benzo	178	151	0	0.00
	Isopropyl	H[a]	269	117	129	2.51
		3-Cl	271	127	119	2.41
		5-Cl	360	127	208	3.19
		3,4-Benzo	415	151	234	3.38
		5,6-Benzo	204	151	23	1.06
	sec-Butyl	H[a]	264	127	112	2.34
		5,6-Benzo	194	161	0	0.00
	t-Butyl	H[a]	613	127	461	4.74
		3-C	1029	136	866	6.50
		5-Cl	655	136	492	4.90
		5,6-Benzo	504	160	312	3.90
Co	Isopropyl	H[a]	596	121	451	4.69
		3-Cl	1017	131	860	6.48
		5-Cl	609	131	452	4.70
		3,4-Benzo	531	155	345	4.10
		5,6-Benzo	513	155	327	4.00
	sec-Butyl	H[a]	595	130	439	4.63
	t-Butyl	H[a]	679	130	523	5.05
		3-Cl	1144	140	976	6.90
		5-Cl	702	140	524	5.11

[a] Cf. ref. 2.

for those assigned as pseudo-tetrahedral. These values are lower than the values found for the tetrahedral tetrahalogen nickel(II) complexes but are in the same range as found for the distorted tetrahedral complexes of the type NiL_2X_2 (X = halogens).[10] This confirms that tetrahedron in these complexes is distorted, as shown by the complete determination by X-rays of the structure of bis(N-isopropylsalicylaldimino)nickel(II),[5] due to the geometry of the ligands.

These results indicate that the repulsion between the bulky t-butyl groups and the oxygen and hydrogen atom (or substituent) at carbon 3 on the other ring is sufficiently large to impose a pseudo-tetrahedral structure on all the N-t-butylsalicylaldiminonickel(II) complexes. With the smaller bulkiness of the linear n-propyl group, however, the planar configuration is stable. The intermediate steric requirements of the α-branched isopropyl and sec-butyl groups cause the energy difference between the planar and tetrahedral configurations to be rather small so that the actual structure is predominantly determined by the electronic and geometric characteristics of the ring substituent and by crystal packing factors.

It is to be noted that the complexes of copper(II) with these substituted salicylaldimines attain the pseudo-tetrahedral structure more easily: for example the 3-methyl and 5-methyl substituted isopropyl derivatives are pseudo-tetrahedral with copper(II) but planar with nickel(II).[11]

Stereochemistry of the Complexes in Solution.— Molecular weight measurements carried out in benzene at 37° by the osmotic method show that the n-propyl and sec-alkyl complexes are not associated (Table I). In freezing benzene, on the other hand, some association was found.[2,12] The absorption spectra of the n-

propyl derivatives show that, in benzene solution at room temperature, they maintain the trans-planar structure found in the solid state[13]; the very low values of the dipole moment in benzene (Table IV) confirm this conclusion. The t-butyl derivatives, however, are pseudo-tetrahedral. The spectra of the benzene solutions show the bands diagnostic of the pseudo-tetrahedral configuration; in particular the band at 6700 cm.$^{-1}$. The magnetic moments, with values ranging from 3.22 to 3.27 B.M., that is, close to those of the solids (Table III), indicate that nickel(II) in these complexes is found predominantly in the triplet state. The high dipole moments (Table IV) are very close to the values of the correspondingcobalt (II) complexes which were found to be tetrahedral,[14] and so confirm the tetrahedral structure.

It is possible to estimate the percentage of tetrahedral molecules in a solution in which only the tetrahedral and planar forms exist from the relationship between the square of the dipole moment of the nickel-(II) complex and that of the corresponding cobalt(II) complex. The same result can be deduced from the square of the magnetic moment measured in solution as compared with the value 3.3 B.M. found for the pure pseudo-tetrahedral complexes: % tetr. = 100 × $\mu_{eff}^2/3.3$,[2] and % tetr. = 100 × $\mu_D^2(Ni)/\mu_D^2(Co)$. In the t-butyl series of complexes the percentages are ca. 90–92% for the 3-Cl, 5-Cl, and the nonsubstituted derivatives. These percentages allow one to calculate the molar extinction coefficients of the tetrahedral species at 6700 cm.$^{-1}$, a region where the planar molecules do not absorb. The molar absorbance ϵ is ca. 42 and from this the percentage of the tetrahedral form in equilibrium with the planar may be calculated: % tetr. = 100 × $\epsilon_{6700}^{max}/42$. For every complex, the

(10) Cf. J. R. Miller, Advan. Inorg. Chem. Radiochem., 4, 154 (1962).

(11) L. Sacconi and M. Ciampolini, J. Chem. Soc., in press.

(12) J. Ferguson, Spectrochim. Acta, 17, 316 (1961); R. H. Holm and T. M. McKinney, J. Am. Chem. Soc., 82, 5507 (1960); R. H. Holm, ibid.,

83, 4683 (1961); R. H. Holm, "Proceedings Sixth International Conference on Coordination Chemistry," S. Kirschner, Ed., The Macmillan Company, New York, N. Y., 1961, p. 344.

(13) E. Frasson, C. Panattoni, and L. Sacconi, J. Phys. Chem., 63, 1908 (1959).

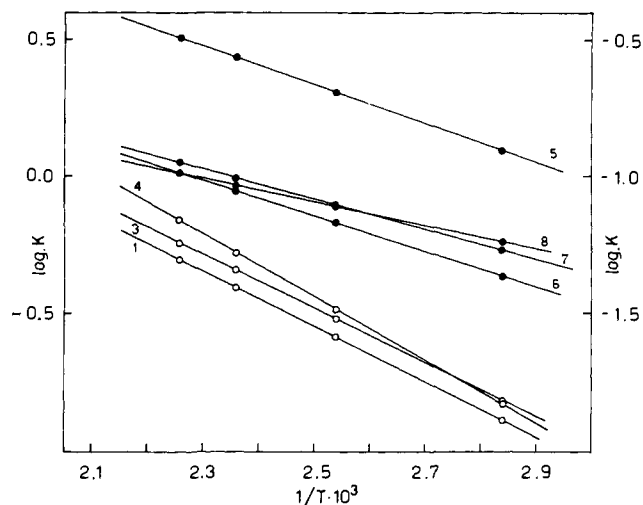(14) L. Sacconi, M. Ciampolini, F. Maggio, and F. P. Cavasino, J. Am. Chem. Soc., 84, 3246 (1962).

Fig. 1.—Plot of log K against $1/T$ for the diamagnetic $\rightleftharpoons$ paramagnetic equilibrium in bis(R-N-alkylsalicylaldimino)nickel(II) chelates: ●, left side scale; O, right side scale (for numerals, see Table V).

values of the percentages of tetrahedral forms calculated from the methods based on dipole moments, magnetic moments, and molar absorbancies are reasonably close. For the 5-chloro isopropyl complex, for example, the values of the percentage of tetrahedral forms at room temperature are: $3.19^2/4.70^2 = 46\%$; $2.17^2/3.3^2 = 43\%$; $19.9/42 = 47\%$, respectively.

At room temperature, the isopropyl and *sec*-butyl complexes in benzene solution, with the exception of the 5,6-benzo derivative, show the bands characteristic of pseudo-tetrahedral species. The molar absorbancies ϵ of the peak at 6700 cm.$^{-1}$ are between 11 and 21 depending on the ring substituent, which indicates that only 25 to 50% of the molecules have this structure. These percentages are also obtained, within experimental error, from the magnetic and electric moments. The isopropyl derivative of 3,4-benzosalicylaldiminonickel(II) (derivative of 1-hydroxy-2-naphthaldehyde) has a dipole moment indicating *ca.* 68% of tetrahedral molecules. However the isopropyl and *sec*-butyl derivatives of 5,6-benzosalicylaldiminonickel(II) (derivative of 2-hydroxy-1-naphthaldehyde) are nonpolar (and therefore *trans*-planar) and have no absorption at *ca.* 6700 cm.$^{-1}$.

Influence of Temperature.—The intensity of the bands at 6700 cm.$^{-1}$ in the spectra of the isopropyl complexes dissolved in *m*-xylene and bibenzyl increases with temperature from 20 to 200°, showing that the percentage of the tetrahedral species increases. In the case of *n*-propyl compounds the band at 6700 cm.$^{-1}$ first appears at *ca.* 80° and the intensity of this band then increases with rising temperature.

Therefore the planar $\rightleftharpoons$ tetrahedral allogonal equilibrium is endothermic in the direction left to right for both the isopropyl and *n*-propyl complexes. With *t*-butyl chelates the molar absorbance ϵ of the peak at 6700 cm.$^{-1}$ diminishes with increasing temperature. Thus, in this case, the formation of the tetrahedral form is exothermic. Some decomposition of these *t*-butyl complexes occurs, however, above 90°.

Approximate values of the thermodynamic functions can be obtained from spectroscopic measurements of the percentages of the tetrahedral form. Above 80°, association is not appreciable and the equilibrium constant may be calculated from

$$K = [\text{tetr.}]/[\text{planar}] = \epsilon_{6700}^{max}/(42 - \epsilon_{6700}^{max})$$

In the range 80–170°, log K varies inversely with temperature (Fig. 1) and thus approximate values of

TABLE V

Thermodynamic Functions for the Planar $\rightleftharpoons$ Tetrahedral Equilibrium of Substituted Bis(R-N-salicylaldimino)-nickel(II) Complexes at 120° in Bibenzyl Solutions

	R	X	ΔF	ΔH	ΔS
			(kcal./mole)		(e.u.)
1	*n*-Propyl	H	2.9	4.6	4
2		3-Cl[a]			
3		5-Me	2.8	4.6	4
4		5-Cl	2.7	5.2	6
5	Isopropyl	H	−0.52	3.2	10
6		3-Cl	0.35	3.0	7
7		5-Me	0.20	2.5	6
8		5-Cl	0.16	2.0	4

[a] No spectrophotometric evidence for the presence of tetrahedral form.

ΔH and ΔS can be calculated. The equilibrium constants for the *t*-butyl complexes cannot be calculated because of the decomposition. The results are summarized in Table V. The differences between the free energies of the planar and pseudo-tetrahedral forms are fairly small. Evidently the steric requirements of the N-alkyl groups are the determining factor affecting the free energy differences between the tetrahedral and the planar forms. The values of the difference are 2.8 to 2.9 kcal./mole for the *n*-propyl derivatives and −0.52 to +0.35 kcal./mole for the isopropyl complexes.

The planar configuration of the *n*-alkyl complexes has an enthalpy of formation 4.6–5.8 kcal./mole less than the enthalpy of formation of the pseudo-tetrahedral configuration. This energy difference is sufficiently large to make the percentage of tetrahedral molecules negligible at room temperature and not greater than 10% even at 170°. The energy difference is reduced to 2.0–3.2 kcal./mole for the isopropyl complexes, surely due to the increased repulsion between the isopropyl group on the one hand and the oxygen and hydrogen atom (or substituent) at carbon 3 of the opposite ring on the other. Thus the percentages of tetrahedral and planar forms are comparable even at room temperature while the tetrahedral form predominates at higher temperatures.

Finally, in the *t*-butyl complexes the repulsions between the bulky *t*-butyl groups and the chelate rings are such that the tetrahedral form has a lower enthalpy of formation than the planar form. Thus the tetrahedral form is more stable at lower temperatures.

The nature and position of substituents on the aromatic ring also affects the free energies of formation of the two stereochemical arrangements. This is clearly seen with the benzo-substituted compounds, where benzo substitution in 3,4-positions has the opposite effect from substitution in 5,6-positions. Benzo substitution in 5,6-positions brought about the most stable planar structure. The *n*-propyl derivative of the 5,6-benzo complex is not only planar in the solid state but also remains exclusively planar at elevated temperatures in solution. The 5,6-benzo isopropyl derivative is also planar as the solid and in solution has the greatest percentage of the planar form of any isopropyl complex either at room temperature or at high temperatures. Benzo substitution in 3,4-positions promotes the formation of the tetrahedral arrangement particularly strongly; in solution the *n*-propyl derivative has the highest proportion of the tetrahedral form of any *n*-propyl complex. The isopropyl 3,4-benzo complex, uniquely among the aromatic ring substituted complexes, is tetrahedral in the solid state. In solution at room temperature it has the greatest percentage of the tetrahedral form of all isopropyl complexes studied. The molar absorbance at

6700 cm.$^{-1}$ of this complex, and thus the percentage of tetrahedral form, is practically independent of temperature, indicating that the energies of formation of planar and tetrahedral allogons are practically equal. For the 3,4-benzo-substituted complexes, the reason for this behavior appears to be essentially steric in nature. Trials with Stuart models, in fact, show a considerable steric interaction between the 3,4-benzo group and the isopropyl group (I). In the case of the 5,6-benzo-substituted complexes (II), the steric reasons do not seem to play any role, and the factors affecting the stereochemistry must be essentially of an electronic nature. The importance of the electronic effects in determining the percentages of tetrahedral species is evident also from the thermodynamic data for the isopropyl complexes in Table V. In fact, the 5-substituted complexes, in which the steric factors do not come into play, have percentages of planar forms, and hence values of ΔF, larger than that of the unsubstituted isopropyl complex. In the case of 3-substitution the influence of electronic factors is even more evident, and while the steric effect of a chloro substituent in position 3 could favor the tetrahedral form, the 3-chloro n-propyl derivative is exclusively planar, even at elevated temperatures. The 3-chloro isopropyl derivative has small percentages of tetrahedral forms, both at and above room temperature.

The differences in entropy of formation between tetrahedral and planar species of n-propyl and isopropyl complexes are always positive in the range 4–10 e.u. The entropy factor favors the attainment of a pseudo-tetrahedral structure, particularly at high temperatures. A part of the entropy difference can be attributed to statistical factors. The ground state of a

I

II
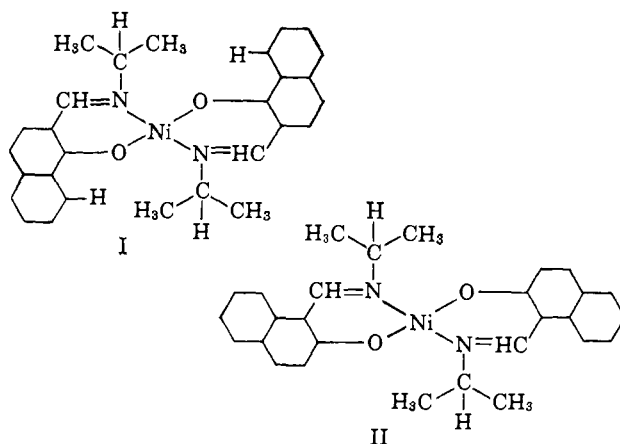
$trans$-planar nickel(II) complex is $^1A_{1g}$ with onefold degeneracy whereas that of a tetrahedral nickel(II) complex is $^3T_1$ with ninefold degeneracy. In a field of pseudo-tetrahedral symmetry the $^3T_1$ level will be split, although the splitting is probably small compared with kT. Therefore a statistical ΔS is expected with a value of approximately $R \ln 9/1 = 4.4$ e.u. Part of the entropy change can also be attributed to the greater freedom of rotation of the alkyl groups in the tetrahedral structure compared with that in the planar structure. Another contribution to the entropy difference may be the greater probability of solvation of the planar species, as in the case of the troponeimine-nickel(II) complexes.[15]

(15) D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *J. Am. Chem. Soc.*, **85**, 397 (1963).

Phosphorus- and Arsenic-Bridged Complexes of Metal Carbonyls. III.[1] Cobalt and Manganese Complexes[2]

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Tetrasubstituted biphosphines react with $Co_2(CO)_8$ to give $[Co\{P(C_6H_5)_2\}(CO)_3]_2$ or $[Co_3\{P(CH_3)_2\}_2(CO)_7]$. $[Mn\{P(C_6H_5)_2\}(CO)_4]_2$ and $[Mn\{As(CH_3)_2\}(CO)_4]_2$ were obtained either from $Mn_2(CO)_{10}$ and the corresponding biphosphine or biarsine or from $NaMn(CO)_5$ and the monochlorophosphine or arsine. $(CH_3)_2PCl$ and $NaMn(CO)_5$ react at room temperature to give $[Mn_2\{P(CH_3)_2\}_2(CO)_9]$, which decomposes to give $[Mn\{P(CH_3)_2\}(CO)_4]_2$ at higher temperature. On the basis of infrared and proton nuclear magnetic resonance spectra, structures containing phosphorus or arsenic bridges are proposed.

We have previously investigated the reactions of the dimeric cyclopentadienyl metal carbonyl compounds of iron, molybdenum, tungsten, and nickel with tetrasubstituted biphosphines and a biarsine, R_4E_2 (E = P, R = CH_3, C_6H_5; E = As, R = CH_3).[1,3] The majority of the complexes which are obtained form part of a series of general formula $[C_5H_5M(ER_2)(CO)_n]_2$ (M = Mo, W, n = 2; M = Fe, n = 1; M = Ni, n = 0), all of which have been shown to contain M_2E_2 heterocyclic rings. It was therefore of interest to study the analogous reactions of the pure metal carbonyls, with the aim of preparing a similar series of complexes. For this purpose we chose to study initially the reactions of the biphosphines and tetramethylbiarsine (cacodyl) with cobalt and manganese carbonyls, since both of these compounds contain metal–metal bonds, a structural feature which appears to facilitate the cleavage

of the phosphorus–phosphorus or arsenic–arsenic bonds in the ligands. Since these carbonyls also form sodium salts, an alternative possible method of synthesis is available by reaction of the salts with the chlorophosphines and -arsines, R_2ECl.

It has previously been reported in a patent that $Co_2(CO)_8$ reacts with tetraphenylbiphosphine, $(C_6H_5)_4P_2$, to give a rose-red compound $(C_6H_5)_4P_2 \cdot 2Co(CO)_3$.[4] The structure of the compound was not discussed but our present reinvestigation indicates structure I. Analogous compounds containing bridging SR groups, $[Co(SR)(CO)_3]_2$, are also known.[5] The corresponding

I

II
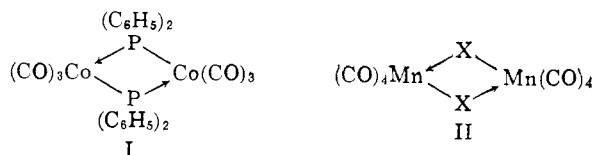
(1) Part II: R. G. Hayter, *Inorg. Chem.*, **2**, 1031 (1963).

(2) Presented in part at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., March 31–April 5, 1963.

(3) R. G. Hayter, *J. Am. Chem. Soc.*, **85**, 3120 (1963).

(4) W. Schweckendiek, German Patent 1,072,244 (Dec. 31, 1959).

(5) W. Hieber and P. Spacu, *Z. anorg. allgem. Chem.*, **233**, 359 (1937).