High-Spin Five-Coordinated 3d Metal Complexes with Pentadentate Schiff Bases

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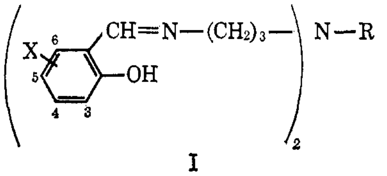
Abstract: The pentadentate Schiff bases formed from substituted salicylaldehydes and bis(3-aminopropyl)amine (X–SalDPT) or bis(3-aminopropyl)methylamine (X–SalMeDPT) form high-spin five-coordinated complexes with manganese(II), cobalt(II), nickel(II), copper(II), and zinc(II) of the general formula (X–SalDPT)M^{II} and (X–SalMeDPT)M^{II}. The stereochemistry of these complexes, both in the solid state and in solution, is discussed on the basis of their magnetic and spectrophotometric properties. The nickel complexes form hexacoordinated adducts with one molecule of pyridine. The thermodynamics of the conformational equilibria between the five-coordinated species and six-coordinated adducts in benzene solution has been studied.

The first high-spin five-coordinated nickel(II) complexes have been described only recently.[1–7] They have been found to have distorted square-pyramidal or trigonal-bipyramidal configurations. The ligands which have been found to give such unusual stereochemistries are Schiff bases derived from salicylaldehyde and N,N-diethylethylenediamine,[1] or methylamine,[3] alkylated polyamines,[5–7] and arsine oxide.[4] The donor atoms (oxygen, nitrogen, halogens) are decidedly electronegative and have a low tendency to form π bonds with the central metal atom. The most suitable ligands are bulky and polydentate. Ligands of this type, in fact, are able to fill the whole space around the metal with a rigid five-coordinated environment so preventing six-coordination. The steric and electronic requirements of the ligands, therefore, play the main role in determining the geometry of these complexes. Crystal-field stabilization effects, which would favor the square-pyramidal structure,[8] are thus to be considered less important.

In order to gain more information on this unusual stereochemistry, we have tried to prepare nickel and other 3d metal complexes with potentially pentadentate ligands. Schiff bases formed from substituted salicylaldehydes and dipropylenetriamines (I), having a set of donor atoms N_3O_2, have been used. These are hereafter indicated as (X–SalDPT) when R = H and as (X–SalMeDPT) when R = CH_3. Complexes of the general formula (X–SalDPT)M^{II} and (X–SalMeDPT)M^{II} with M = Mn, Co, Ni, Cu, or Zn have been obtained.



I

Values of the magnetic susceptibility of some of these compounds have already been reported by Calvin, *et al.*,[9] without any other detail, in the course of their investigation of the oxygen-carrying capacity of the cobalt chelates. The preparation of some cobalt complexes has also been reported.[10]

Experimental Section

Preparation of the Compounds. The nickel(II) and copper(II) complexes were prepared by adding a solution of the appropriate dipropylenetriamine (10 mmoles) in 15 ml of ethanol to a suspension in 50 ml of ethanol of bis(salicylaldehydato)metal(II) dihydrate (10 mmoles). The cobalt(II), manganese (II), and zinc(II) compounds were prepared by adding a solution of metal acetate (10 mmoles) in 15 ml of water to a solution of dipropylenetriamine (10 mmoles) and X-salicylaldehyde (20 mmoles) in 50 ml of ethanol. In both cases the reaction mixture was heated under reflux for 0.5 hr, and water was added in order to facilitate the precipitation. After cooling the reaction mixture, the precipitate was collected and recrystallized. The cobalt and manganese compounds were prepared and collected under a nitrogen atmosphere in order to avoid oxidation. The colors of the compounds are: nickel, green; manganese, orange to yellow; cobalt, yellow; copper, green; zinc, white. The adduct (H–SalDPT)Ni·py was prepared by adding petroleum ether to a solution of (H–SalDPT)Ni^{II} in chloroform containing an excess of pyridine. The compound was dried in a desiccator over KOH in presence of liquid pyridine.

Anal. Calcd for $C_{25}H_{28}N_4O_2Ni$: N, 11.78; Ni, 12.35. Found: N, 11.86; Ni, 12.27.

Physical Measurements. The absorption spectra were recorded with a Beckman DK2 spectrophotometer. The solvents were purified by the standard procedures used for spectrophotometric measurements. The pyridines, which were good quality commercial products (Fluka), were purified until their physical properties agreed closely with the values in the literature. Usually they were refluxed over potassium hydroxide or barium oxide and fractionated through a Vigreux column; the constant-boiling middle fractions were collected. The solutions of the bases in benzene were prepared by weight. The reflectance spectra were recorded using the standard Beckman reflectance attachment and magnesium oxide as a reference. Concentrations of the solutions were in the range 0.01–0.02 *M*. Absorption spectra for equilibria studies were measured with a Beckman DU quartz spectrophotometer fitted with a thermostated cell compartment. The solutions used contained 10^{-4} mole/l. of the complex and known and varying amounts of pyridine. The solution used as a blank contained the same concentration of base as the sample.

The magnetic susceptibility measurements were performed by the Gouy method, with the apparatus and the experimental technique described in a previous paper.[11] The sample tube was calibrated

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(1) L. Sacconi, P. Nannelli, N. Nardi, and U. Campigli, *Inorg. Chem.*, 4, 943 (1965).

(2) L. Sacconi, P. L. Orioli, and M. Di Vaira, *J. Am. Chem. Soc.*, **87**, 2059 (1965).

(3) L. Sacconi, M. Ciampolini, and G. P. Speroni, *ibid.*, **87**, 3102 (1965).

(4) J. Lewis, R. S. Nyholm, and S. A. Rodley, *Nature*, **207**, 72 (1965).

(5) M. Ciampolini and N. Nardi, *Inorg. Chem.*, **5**, 41 (1966).

(6) M. Ciampolini and G. P. Speroni, *ibid.*, **5**, 45 (1966).

(7) Z. Dori and H. B. Gray, *J. Am. Chem. Soc.*, **88**, 1394 (1966).

(8) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p 55.

(9) M. Calvin and C. H. Barkelew, *J. Am. Chem. Soc.*, **68**, 2267 (1946); O. L. Harle and M. Calvin, *ibid.*, **68**, 2612 (1946), and references therein.

(10) R. H. Bailes and M. Calvin, *ibid.*, **69**, 1886 (1947).

Table I. Summary of Physical and Analytical Data for (X–SalDPT)M^{II} and (X–SalMeDPT)M^{II} Complexes

Compound	Formula	Crystallization	Mp, °C	Calcd, %		Found, %	
				N	M	N	M
(H–SalDPT)Ni	$C_{20}H_{23}N_3O_2Ni$	$CHCl_3$ + petr ether	271–273	10.61	14.82	10.58	14.61
(5-Cl–SalDPT)Ni	$C_{20}H_{21}Cl_2N_3O_2Ni$	C_6H_6	272–275	9.04	12.62	9.08	12.66
(5-CH_3–SalDPT)Ni	$C_{22}H_{27}N_3O_2Ni$	C_6H_6	240–241	9.91	13.84	9.77	13.93
(5-Br–SalDPT)Ni	$C_{20}H_{21}Br_2N_3O_2Ni$	C_6H_6 + cyclohexane	266–269	7.59	10.59	7.60	10.56
(5-C_2H_5–SalDPT)Ni	$C_{24}H_{31}N_3O_2Ni$	C_6H_6 + cyclohexane	201–203	9.29	12.98	9.39	12.81
(3-Cl–SalDPT)Ni	$C_{20}H_{21}Cl_2N_3O_2Ni$	C_6H_6 + cyclohexane	273–276	9.04	12.63	9.08	12.69
(3-CH_3–SalDPT)Ni	$C_{22}H_{27}N_3O_2Ni$	C_6H_6 + cyclohexane	222–225	9.91	13.84	9.80	13.79
(3,5-Cl_2–SalDPT)Ni	$C_{20}H_{19}Cl_4N_3O_2Ni$	C_2H_5OH	210–214	7.87	10.99	7.89	10.94
(3,4-Benzo–SalDPT)Ni	$C_{28}H_{27}N_3O_2Ni$	C_6H_6 + C_2H_5OH	307–310	8.47	11.80	8.40	11.91
(5,6-Benzo–SalDPT)Ni	$C_{28}H_{27}N_3O_2Ni$	C_6H_6 + C_2H_5OH	320–323	8.47	11.80	8.41	11.73
(H–SalMeDPT)Ni	$C_{21}H_{25}N_3O_2Ni$	C_6H_6 + cyclohexane	270–275	10.25	14.31	10.24	14.22
(5-Cl–SalMeDPT)Ni	$C_{21}H_{23}Cl_2N_3O_2Ni$	C_6H_6 + cyclohexane	305–308	8.77	12.25	8.93	12.34
(5-CH_3–SalMeDPT)Ni	$C_{23}H_{29}N_3O_2Ni$	C_6H_6 + cyclohexane	234–237	9.59	13.39	9.65	13.37
(5-Br–SalMeDPT)Ni	$C_{21}H_{23}Br_2N_3O_2Ni$	$CHCl_3$ + petr ether	286–289	7.39	10.33	7.37	10.40
(3-Cl–SalMeDPT)Ni	$C_{21}H_{23}Cl_2N_3O_2Ni$	$CHCl_3$ + C_2H_5OH	290–293	8.77	12.25	8.80	12.25
(3-CH_3–SalMeDPT)Ni	$C_{23}H_{29}N_3O_2Ni$	C_6H_6 + cyclohexane	244–248	9.59	13.39	9.43	13.30
(3,5-Cl_2–SalMeDPT)Ni	$C_{21}H_{21}Cl_4N_3O_2Ni$	C_6H_6 + cyclohexane	256–260	7.67	10.71	7.71	10.90
(H–SalDPT)Co	$C_{20}H_{23}N_3O_2Co$	C_2H_5OH + H_2O		10.60	14.87	10.36	14.92
(5-Cl–SalDPT)Co	$C_{20}H_{21}Cl_2N_3O_2Co$	C_2H_5OH		9.03	12.67	9.05	12.50
(H–SalMeDPT)Co	$C_{21}H_{25}N_3O_2Co$	C_2H_5OH		10.24	14.36	10.20	14.51
(5-Cl–SalMeDPT)Co	$C_{21}H_{23}Cl_2N_3O_2Co$	C_2H_5OH		8.77	12.30	8.85	12.21
(H–SalDPT)Cu	$C_{20}H_{23}N_3O_2Cu$	$CHCl_3$ + petr ether	235–237	10.48	15.85	10.48	16.14
(H–SalMeDPT)Cu	$C_{21}H_{25}N_3O_2Cu$	$CHCl_3$ + petr ether	235–238	10.13	15.31	10.29	15.79
(H–SalDPT)Mn	$C_{20}H_{23}N_3O_2Mn$	$CHCl_3$ + petr ether		10.71	14.00	10.42	14.31
(5-Cl–SalMeDPT)Mn	$C_{21}H_{23}Cl_2N_3O_2Mn$	C_2H_5OH		8.84	11.56	8.96	11.80
(H–SalDPT)Zn	$C_{20}H_{23}N_3O_2Zn$	$CHCl_3$ + petr ether	263–265	10.43	16.23	10.53	15.86
(H–SalMeDPT)Zn	$C_{21}H_{25}N_3O_2Zn$	$CHCl_3$ + petr ether	245–247	10.08	15.68	10.29	15.41

Table II. Magnetic Data for Some (X–SalDPT)M^{II} and (X–SalMeDPT)M^{II} Complexes[a]

Compound	State	Temp, °C	$\chi_g \times 10^6$	$\chi_M \times 10^6$	μ_{eff}, BM
(H–SalDPT)Ni	Solid	21	11.76	4876	3.40
	$CHCl_3$	20	10.98	4582	3.30
	o-$Cl_2C_6H_4$	150	7.91	3342	3.37
(H–SalMeDPT)Ni	Solid	20	10.53	4691	3.34
(H–SalDPT)Co	Solid	21	18.95	7720	4.28
(5-Cl–SalMeDPT)Co	Solid	21	16.70	8261	4.41
(H–SalDPT)Cu	Solid	21	3.35	1578	1.93
	$CHCl_3$	21	3.10	1477	1.87
(H–SalMeDPT)Cu	Solid	22	2.77	1395	1.82
(H–SalDPT)Mn	Solid	25	36.38	14447	5.90

[a] The $\chi_M \times 10^6$ values at 25° found by Calvin are: (H–SalDPT)Ni, 4450; (H–SalDPT)Co, 7700; (H–SalDPT)Cu, 810.

with Hg(Co(NCS)$_4$)[12] and freshly boiled distilled water.[12] Diamagnetic corrections were calculated from Pascal's constants.[13]

Results

The analytical data and characteristics of the complexes (X–SalDPT)M^{II} and (X–SalMeDPT)M^{II} with M = Mn, Co, Ni, Cu, or Zn are reported in Table I. The Cu, Ni, and Zn compounds are stable in the solid state and in solution, while the Co and Mn complexes have a strong tendency to oxidize, especially in solution, and can only be preserved in an inert atmosphere.

The magnetic susceptibilities of the compounds have been measured both in the solid state and in solution (Table II). The complexes from Mn to Cu are all high-spin. In all cases the magnitude of the orbital contribution to the magnetic moment is rather small. The magnetic moments of the nickel compounds, ranging from 3.30 to 3.45 BM, are slightly higher than those usually found for regular octahedral complexes. The magnetic moments of these complexes dissolved in inert solvents are practically identical with those of the solids. The magnetic susceptibilities of the (H–SalDPT)Mn^{II} and (H–SalMeDPT)Ni^{II} complexes have been measured at various temperatures between 80 and 295°K. The temperature dependence of the magnetic susceptibility obeys the Curie–Weiss law with a Weiss constant $\theta \simeq 0$°K, indicating the absence of intermolecular interactions.

Spectrophotometric measurements of these compounds in the crystal-field region have been performed in the solid state as well as in solution. The frequencies of the absorption maxima and the molar absorbancies of some typical complexes are reported in Table III. The spectra of the solids are not significantly different from those in solution in inert solvents like $CHCl_3$ or C_6H_6 (Figures 1 and 2), although some minor variations in the frequencies of the absorption maxima have been observed when the solvent was changed from CS_2 to CH_3CN *via* CCl_4, $CHCl_3$, and CH_2Cl_2. No evident relation has, however, been found between absorption frequency and solvent properties. The absorption spectra of the Co and Cu complexes in pyridine solution are not appreciably different from those in the solid state (Figures 3 and 4). For the nickel complexes, on the contrary, the reflectance spectra are different from the absorption spectra in pyridine (Figure 5). At different concentrations of pyridine these spectra in benzene show three isosbestic points (at 10,870, 13,330, and 18,850 cm^{-1}) (Figure 5), indicative of equilibria between such complexes and their pyridine adducts. A monoadduct with formula (H–SalDPT)Ni·py has been also prepared. Its reflectance spectrum is practically identical with the absorption spectrum of (H–SalDPT)Ni^{II} in pyridine.

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

(12) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and L. Wilkins, Ed., Interscience Publishers Inc., New York, N. Y., 1960, p 415.

(13) *Cf.* P. W. Selwood, "Magnetochemistry," 2nd ed, Interscience Publishers Inc., New York, N. Y., 1956.

Table III. The Maxima and Extinction Coefficients for the Electronic Spectra of the Complexes

Compound	State	Absorption max, cm^{-1} (ϵ_{molar} for soln)
(H-SalDPT)Ni	Solid	<5000, 8930, 10,500 sh, 11,800 sh, 17,200, 22,200 sh
	$CHCl_3$	<5000, 8850 (26.2), 9800 sh, 11,810 (6.7), 17,000 (26)
	Pyridine	10,000 sh, 11,500 (11.6), 18,300 sh.
(H-SalDPT)Ni·py	Solid	10,000 sh, 11,500, 18,870 sh
(H-SalMeDPT)Ni	Solid	<5000, 8500, 9700 sh, 11,500 sh, 16,400
	$CHCl_3$	<5000, 8500 (39), 10,000 sh, 11,800 (13), 16,700 (69.5)
	Pyridine	9350 (8.9), 11,400 (9.0), 18,100 sh
(H-SalDPT)Co	Solid	6100, 15,600 sh
(H-SalMeDPT)Co	Solid	6580, 15,150 sh
	$CHCl_3$	6330 (12), 14,700 (26)
	Pyridine	6350 (9), 14,700 (23)
(H-SalDPT)Cu	Solid	10,200 sh, 12,500
	$CHCl_3$	12,350 (213)
	Pyridine	12,350 (253)
(H-SalMeDPT)Cu	Solid	11,000 sh, 12,270
(H-SalDPT)Mn	Solid	21,000 sh, 24,400
(5-Cl-SalMeDPT)Mn	Solid	21,000 sh, 26,300

The spectra of N–H and N–CH_3 derivatives of each metal in the 5000–20,000-cm^{-1} region are very similar (Figures 1, 3, and 4). They show only a displacement of the frequencies of the peaks toward lower energies in the case of the N–CH_3 derivatives. This displacement can be correlated with the relative position of the secondary and tertiary amine nitrogens in the spectrochemical series.[14] No appreciable variation of the spectra is observed when the X substituents are changed in each series of complexes.

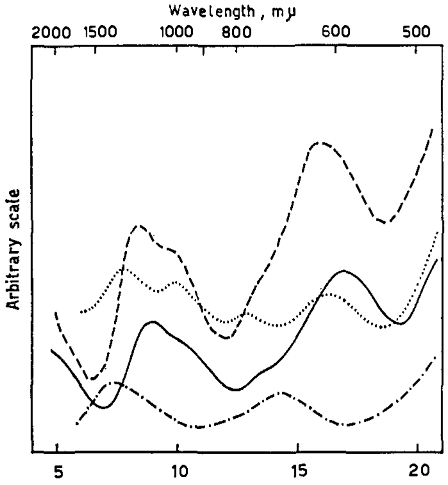

Figure 1. Reflectance spectra of (H-SalDPT)Ni (———), (H-SalMeDPT)Ni (– – – –), (5-Cl-Sal(en)-N(C_2H_5)$_2$)$_2$Ni (. . . .), and bis(N-methylsalicylaldiminato)nickel (- · · · -).

The infrared spectra of the (X-SalDPT)M^{II} complexes show a medium–weak sharp band at 3250 cm^{-1} which may be assigned to N–H stretching. The value of this frequency is low when compared with those reported for secondary amines.[15] Since sharpness of this band excludes the presence of hydrogen bonds, the lowering of its frequency must be attributed to the metal–nitrogen coordination bond.

X-Ray powder photographs have been taken for the series of (H-SalDPT)M^{II} and (H-SalMeDPT)M^{II} complexes. The DPT compounds show two types of patterns: one for Ni, Cu, and Zn, the other for Co and Mn complexes. The photographs of the MeDPT derivatives are practically indistinguishable among each other.[16]

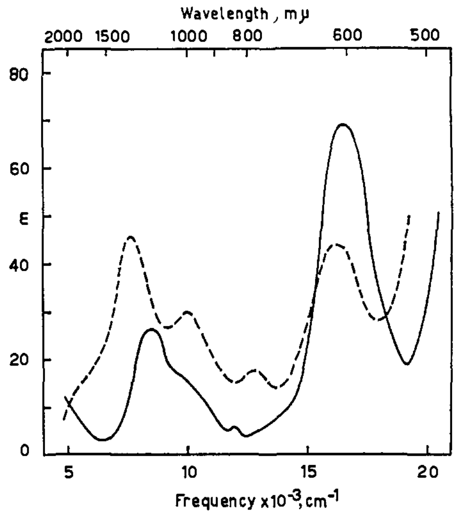

Figure 2. Absorption spectra in $CHCl_3$ solution of (H-SalMeDPT)Ni (———) and (5-Cl-Sal(en)-N(C_2H_5)$_2$)$_2$Ni (– – – –).

Discussion

The (H-SalMeDPT)M^{II} complexes are all isomorphous.[16] For a given metal, both the DPT and MeDPT complexes have similar reflectance spectra, independently of the X substituent at the salicylaldimine ring. Thus the same stereochemistry must be assigned to all the solid compounds listed in Table I. The differences between the X-ray powder photographs of the (H-SalDPT)M^{II} complexes of Ni, Cu, and Zn and those of Co and Mn can therefore be attributed to differences in the packing of the molecules in the crystal rather than to substantial differences in the stereochemistry of the complexes. Molecular weight measurements on some nickel complexes in benzene solution show that these compounds are monomeric. These results and the

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(14) S. F. Pavkovic and D. W. Meek, *Inorg. Chem.*, 4, 20 (1965).

(15) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1960, p 250.

(16) The complex (H-SalMeDPT)Mn^{II} has been isolated, but it decomposes too rapidly to allow physical measurements. The (5-Cl-SalMeDPT)Mn^{II} complex is isomorphous with the cobalt analog.

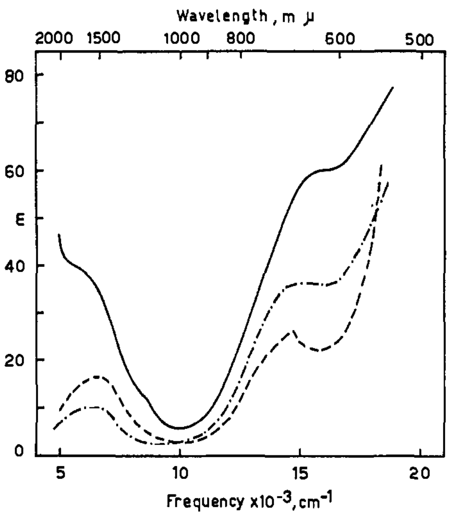


Figure 3. Reflectance spectra of (H-SalDPT)Co (———) and H-SalMeDPT)Co (- - - -), arbitrary scale; absorption spectrum of (H-SalMeDPT)Co in pyridine solution (- · · · -).

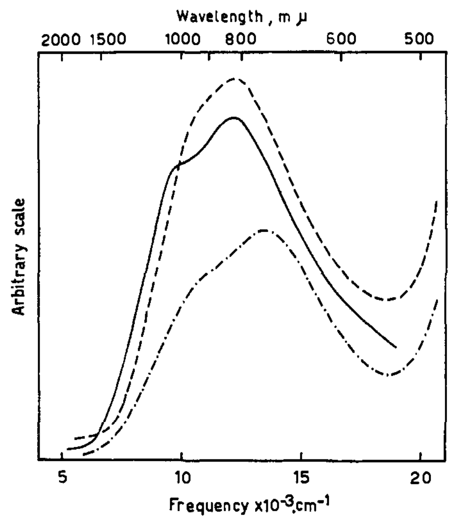
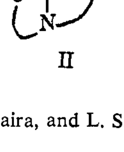


Figure 4. Reflectance spectra of (H-SalDPT)Cu (———), (H-SalMeDPT)Cu (- - - -), and bis(N-methylsalicylaldiminato)copper (- · · · -).

similarity of the spectra of the complexes in the solid state and in solution lead us to conclude that these compounds are always present as monomeric molecules which may be formulated as $(X\text{-}SalDPT)M^{II}$ and $(X\text{-}SalMeDPT)M^{II}$. Furthermore the infrared measurements on the N-H derivatives indicate that the nitrogen of the amino group is also linked to the metal. We can conclude therefore that these complexes are five-coordinated. These compounds are the first five-coordinated complexes of 3d metals with a single pentadentate ligand so far described.

The spectral and magnetic data are in accordance with a high-spin five-coordinated structure. In fact, the crystal-field spectra of these complexes are similar to those of other high-spin complexes to which the five-coordinated structure has been attributed through physical measurements or has been shown by X-ray crystallography. In particular the spectra of the nickel complexes are similar to the spectrum[1] of the complex (5-Cl-Sal(en)-N(C_2H_5)$_2$)$_2$Ni which has the same set of donor atoms (N_3O_2) and which has been shown to have a distorted square pyramidal structure.[2] Moreover they are also similar to the spectrum of the complex bis(N-methylsalicylaldiminato)nickel, with an N_2O_3 set of donor atoms, which exhibits a distorted trigonal bipyramidal configuration when it is guest in the lattice of the zinc analog[3] (see Figures 1 and 2).

Preliminary data from a three-dimensional X-ray analysis[17] on the compound $(H\text{-}SalMeDPT)Ni^{II}$, still in progress in this laboratory, show that the nickel is five-coordinated and that the geometry of the donor atoms is intermediate between that of the trigonal bipyramid and the square pyramid (II).



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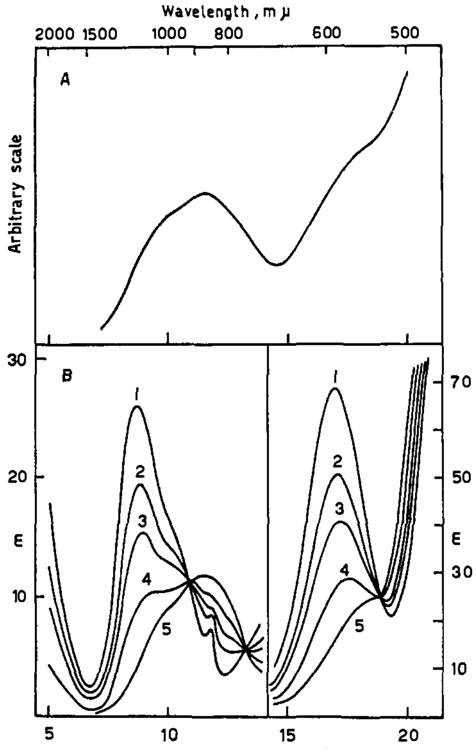

Figure 5. Reflectance spectrum of the adduct (H-SalDPT)Ni·py (curve A). Absorption spectra of (H-SalDPT)Ni in solution at 25° (curves B): (1) in benzene; (5) in pyridine; (2-4) in pyridine-benzene mixtures.

The two nitrogens of the azomethine groups are in the axial positions; the nitrogen of the amino group and the two oxygen form the equatorial triangle which is normal to the N-Ni-N axis. The angle O-Ni-O is near 142°.

Recently, the splitting of the terms of the free nickel(II) ion in crystal fields of D_{3h} symmetry (trigonal bipyramidal) and C_{4v} symmetry (square-pyramidal configuration with the nickel ion lying in the basal plane or above it) has been calculated.[18] It has been shown

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(17) P. L. Orioli, M. Di Vaira, and L. Sacconi, *Chem. Commun.*, 300 (1966).

(18) M. Ciampolini, *Inorg. Chem.*, 5, 35 (1966).

that in five-coordinated configurations the terms of the nickel(II) ion split into a relatively high number of terms, as may be expected because of the lower symmetry of these configurations compared with that of tetrahedral or octahedral configurations. As a consequence, small geometrical distortions and/or ligand nonequivalence are capable of inverting the order of the energy of the terms which arise from the nickel(II) ion. Presumably, this may account for the fact that the frequencies of the absorption peaks for the (X-SalDPT)Ni^{II} and (X-SalMeDPT)Ni^{II} complexes are only roughly in accordance with the calculated frequencies for the two configurations. It is, however, interesting to note that for a similar set of donor atoms in a regular trigonal bipyramidal configuration only one band is expected in the near-infrared region at *ca.* 7000 cm^{-1}, while two bands are expected for a regular square-pyramidal configuration, one at 7200 cm^{-1} and the other at *ca.* 10,800 cm^{-1}. The spectra of the (5-Cl-Sal(en)-N(C$_2$H$_5$)$_2$)$_2$Ni and bis(N-methylsalicylaldiminato)nickel complexes are in satisfactory agreement with these predictions.[18] In the near-infrared region the spectra of the (X-SalDPT)Ni^{II} and (X-SalMeDPT)Ni^{II} complexes show a band at 8500 cm^{-1} with a shoulder at *ca.* 9500-10,000 cm^{-1}. The features of these spectra are significantly intermediate between those of the above-mentioned complexes, as may be expected for a configuration of type II. Moreover, the absorption band at about 5000 cm^{-1} closely resembles both in shape and frequency the band shown by the complex Ni(denMe)X$_2$[6](denMe = CH$_3$N-(CH$_2$CH$_2$N(CH$_3$)$_2$)$_2$ and X = Cl, Br, or I) which has been assigned a pentacoordinated structure, probably intermediate between the square pyramid and the trigonal bipyramid.

The spectra of the (X-SalDPT)Co^{II} and (X-SalMeDPT)Co^{II} complexes show a low absorption at *ca.* 5000-6000 cm^{-1} and a band at *ca.* 15,000-16,000 cm^{-1} (see Figure 3). The latter band often appears as a shoulder of a strong absorption band which is probably due to a ligand-ligand or charge-transfer transition. Spectra of this type are completely different from those of tetrahedral or octahedral cobalt(II) complexes with salicylaldimines. The observed bands closely resemble those of bis(N-methylsalicylaldiminato)cobalt[3] and [Co(trenMe)X]X[5] complexes (trenMe = N(CH$_2$CH$_2$N-(CH$_3$)$_2$)$_3$ and X = Cl, Br, or I), which both have a trigonal bipyramidal configuration. The spectra of these last two complexes show, however, another band at *ca.* 12,000 cm^{-1}. This is presumably due to some differences in the geometry of the pentacoordinated structures. The spectra of the cobalt(II) complexes studied here are similar to that of the adduct of bis(N-2,6-dimethylphenylsalicylaldiminato)cobalt with a molecule of pyridine to which a pentacoordinated structure has been attributed.[19] As it has been pointed out in the introduction, the preparation of (H-SalMeDPT)-Co^{II} and of some (X-SalDPT)Co^{II} complexes and the measurements of their magnetic susceptibilities have previously been reported by Calvin in the course of his studies on oxygen-carrying complexes. On account of their oxygen-carrying capacity, he suggested[9] in 1946 for these complexes a pentacoordinated square-pyramidal configuration.

The spectra of (X-SalDPT)Cu^{II} and (X-SalMeDPT)-Cu^{II} complexes (Figure 4) are also typical of five-coordinated structures. They show a broad band with a shoulder at 10,500 and a maximum at 12,300 cm^{-1}. The absorption frequencies can be correlated with the bands at 12,000 and 13,500 cm^{-1} present in the spectrum of the five-coordinated bis(N-methylsalicylaldiminato)-copper[3] and with those at 10,000 and 13,000 cm^{-1} in the spectrum of [Cu(trenMe)X]X,[5] which also has a trigonal bipyramidal configuration.

The behavior of these (X-SalDPT)M^{II} and (X-SalMeDPT)M^{II} complexes toward pyridine is of further interest. The nickel complexes form six-coordinated adducts with one molecule of pyridine both in the solid state and in solution. The spectra of these adducts (Figure 5) show one band and a shoulder (or two peaks) in the 9000-12,000-cm^{-1} region and a shoulder at *ca.* 18,500 cm^{-1} indicative of distorted octahedral configurations. Surprisingly, the spectra of the cobalt complexes dissolved in pyridine are similar to those of the solids, indicating that the pyridine does not coordi-

Table IV. Formation Constants and Thermodynamic Functions for the Equilibrium Reactions between (X-SalDPT)Ni^{II} or (X-SalMeDPT)Ni^{II} and Pyridine in Benzene Solution[a]

Compound	Temp, °C	Log *K*	ΔG, kcal/mole	ΔH, kcal/mole	ΔS, eu
(H-SalDPT)Ni	10	2.07	−2.48	−6.7	−14
	20	1.92			
	25	1.82			
	35	1.65			
	45	1.51			
(5-C$_2$H$_5$-SalDPT)Ni	10	1.94	−2.26	−7.6	−18
	20	1.78			
	25	1.66			
	35	1.48			
	45	1.30			
(5-Cl-SalDPT)Ni	10	2.53	−3.06	−7.6	−15
	20	2.35			
	25	2.25			
	35	2.06			
	45	1.88			
(5-Br-SalDPT)Ni	10	2.64	−3.18	−7.9	−16
	20	2.43			
	25	2.33			
	35	2.15			
	45	1.97			
(3,4-Benzo-SalDPT)Ni	10	2.76	−3.32	−7.9	−15
	20	2.58			
	25	2.44			
	35	2.26			
	45	2.09			
(5,6-Benzo-SalDPT)Ni	10	2.72	−3.34	−7.1	−12
	20	2.54			
	25	2.46			
	35	2.28			
	45	2.12			
(H-SalMeDPT)Ni	10	1.56	−1.84	−5.5	−12
	20	1.42			
	25	1.35			
	35	1.22			
	45	1.09			
(5-Br-SalMeDPT)Ni	10	2.21	−2.59	−8.1	−18
	20	2.02			
	25	1.91			
	35	1.71			
	45	1.53			

[a] The accuracy of the thermodynamic functions is as follows: ΔG, ±0.06 kcal/mole; ΔH, ±0.4 kcal/mole; ΔS, ±1.5 eu.

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(19) Yamada and H. Nishikawa, *Bull. Chem. Soc. Japan*, 38, 683 (1965).

nate to metal. Also the copper complexes behave in the same manner. This indicates a greater tendency of copper and cobalt to give five-coordinated, rather than six-coordinated, complexes in comparison with nickel. The apparently contradictory properties of these cobalt complexes to exhibit the oxygen-carrying capacity,[9] but not the tendency to add pyridine, seems, however, to be worthy of further study.

Equilibria between the Nickel and Pyridine Complexes. In solution of inert solvents the (X–SalDPT)Ni^{II} and (X–SalMeDPT)Ni^{II} complexes give rise with pyridine to equilibria of the type

$$\underset{\text{five-coordinated}}{\text{(X-SalDPT)Ni}} + \text{py} \rightleftarrows \underset{\text{six-coordinated}}{\text{(X-SalDPT)Ni}\cdot\text{py}}$$

The different absorption characteristics of the two coordination compounds allow a spectrophotometric study of these equilibria. The equilibrium constants for the formation reactions of the adducts in benzene at different temperatures have been determined using a method described elsewhere.[20] From the temperature dependence of these constants the enthalpy and entropy changes have been calculated and are reported in Table IV. This is the first thermodynamic study of an equilibrium between high-spin five-coordinated and six-coordinated nickel complexes.

All the formation reactions of the adducts are exothermic, as shown by the values of ΔH from -5.5 to -8.8 kcal/mole. Both the ΔH and ΔS values ($\Delta S = -12$ to -18 eu) are about half of those found for the planar ⇆ octahedral equilibrium between NiDBH and two molecules of pyridine in benzene where $\Delta H = -14.9$ kcal/mole and $\Delta S = -32.9$ eu. If ΔH is regarded as a measure of the bond energy between the central nickel and the pyridine nitrogen, the data presented in the present work indicate that the bond energy Ni–py is approximately the same for (X–SalDPT)Ni·py as for the biadduct NiDBH·2py.

The dependence of the free-energy changes on the X substituents indicates that the tendency of the nickel complexes to achieve the octahedral configuration increases in the order: 5-C_2H_5, H, 5-Cl, 5-Br, 3,4-benzo, 5,6-benzo. It is difficult to give an explanation of this order on the basis of the electronic and steric requirements of the substituents. It is nevertheless interesting to note that in the conformational equilibria between planar diamagnetic and paramagnetic (pentacoordinate,[1] hexacoordinate,[21] or tetrahedral[22]) forms of nickel complexes with Schiff bases, the 5-Cl and 3,4-benzo substituents mostly favor the paramagnetic from while the 5,6-benzo substituent favors the planar diamagnetic form. In the equilibrium between paramagnetic forms no substantial difference is found between 3,4- and 5,6-benzo substituents.

The higher free-energy changes in the formation reaction of the six-coordinated adducts of DPT derivatives compared with the MeDPT derivatives can be explained by considering that the bonding of the pyridine to the nickel involves the compression of the ligands. In this way the methyl group will probably exert a higher steric hindrance than the hydrogen atom to the rearrangement of the complex.

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