ence of air and alcohol or by thermolysis.[16] Nucleophilic attack at the 4 position is consistent with calculated π-electron charge densities for azulene.[17] MO calculations for dithiotropolone and its anion[18] indicate positive π-charge density at each carbon but do not indicate preferential electrophilicity at the α position. Calculations for $M(SST)_2$ complexes have not been carried out.

Finally, it is observed that, although the formation of the anions **6**, **9**, and $[Zn(H,Me\text{-}SST)_2]^{2-}$ is consistent with direct nucleophilic addition, a process involving reduction of $M(SST)_2$ to $M(SST)_2\cdot^-$ followed by reaction with methyl radicals cannot be completely discounted. However, this process is regarded as less probable for at least two reasons. First, only one positional isomer was detected in appreciable quantity; it is not clear why a radical process would not give appreciable amounts of more than one isomer. Second, numerous extremely careful attempts[19] to generate radical anions by electrochemical and chemical reductions have never resulted in the formation of any epr-detectable species, even under conditions where relatively short-lived species would have been observable. In this connection it is noted that the failure to detect the epr signal of the naphthalenide ion during the reaction of naphthalene with *tert*-butyllithium has been taken as sound evidence for direct addition of RLi to the hydrocarbon.[20]

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CONTRIBUTION FROM THE LABORATORIO C.N.R. AND ISTITUTO DI CHIMICA GENERALE ED INORGANICA, UNIVERSITÀ DI FIRENZE, 50132 FLORENCE, ITALY

Synthesis, Characterization, and Proton Magnetic Resonance Spectra of Nickel(II) and Cobalt(II) Complexes with *o*-Mercaptobenzaldiminates

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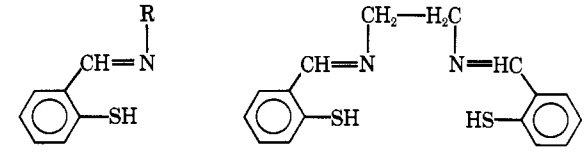
Nickel(II) and cobalt(II) complexes with Schiff base ligands formed from *o*-mercaptobenzaldehyde and mono- or polyamines having donor sets SN, S_2N_2, and S_2N_3, have been prepared and characterized. Planar, tetrahedral, and pentacoordinate complexes have been obtained. The stereochemistry and the solution behavior of these complexes have been compared with those of the analogous salicylaldiminate complexes. Among the bis-bidentate complexes the sulfur atoms favor the low-spin planar stereochemistry in comparison with the oxygen atoms. Pmr spectra of the pentacoordinate nickel complexes indicate the occurrence of an intramolecular interconversion involving the aromatic fragments and the Ni–S bonds. With this in mind the origin of the signal splitting observed for the analogous salicylaldiminate complexes is reconsidered.

Introduction

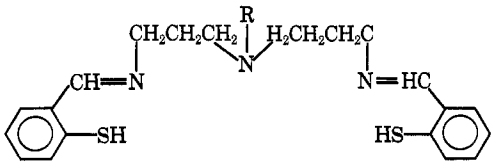
It is well known that Schiff base ligands obtained from salicylaldehyde and mono- or polyamines (having donor sets ON, O_2N_2, O_2N_3, and O_2N_4) give rise to nickel(II) and cobalt(II) complexes with coordination numbers 4, 5, and 6.[1,2] Such complexes have been defined labile[2] in the sense that they may interconvert into complexes with different stereochemistries depending on the substituent group of the aromatic ring and on the synthesis conditions, *e.g.*, solvent, temperature, and presence of a different metal ion whose complex lattice may host the nickel or cobalt complex.[3] In solution many conformational equilibria have been described and, for some of them, the thermodynamic functions have been determined.[1,2]

The present paper deals with nickel(II) and cobalt(II) complexes with Schiff base ligands analogous to the above ligands but with the sulfur atoms substituting the oxygen atoms. Such ligands having donor sets SN, S_2N_2, and S_2N_3 have been obtained from *o*-mercaptobenzaldehyde (TIB) and various amines as shown below



TIB-R, R = Me
R = Et
R = *i*-Pr
R = *sec*-Bu
R = *tert*-Bu

TIB-en



TIB-DPT, R = H
TIB-MeDPT, R = Me

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TABLE I
ANALYTICAL DATA AND PHYSICAL PROPERTIES OF THE COMPLEXES

Compd	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found	% metal Calcd	% metal Found	% S Calcd	% S Found	$\bar{n}$[a]	μ_{eff}, BM (°C)
NiTIB-*N*-Me	53.51	53.90	4.49	4.80	7.80	7.62					1.0	Diam
NiTIB-*N*-Et	55.83	56.05	5.21	5.50	7.23	7.34					0.97	Diam
NiTIB-*N*-*i*-Pr	57.85	57.90	5.83	6.00	6.75	6.51	14.14	14.05	15.44	15.25	0.96	Diam
NiTIB-*N*-*sec*-Bu	59.60	60.10	6.37	6.60	6.32	6.33					0.98	Diam
NiTIB-N-*tert*-Bu	59.60	59.90	6.37	6.60	6.32	6.49	13.24	13.24	14.47	14.00	0.97	3.15 (20)
NiTIB-en[b]	53.81	53.80	3.95	3.82	7.84	7.81					1.04	Diam
NiTIB-DPT	56.09	55.61	5.41	5.47	9.81	9.74	13.71	13.81	14.97	14.70	0.98	3.25 (24)
NiTIB-MeDPT	57.02	56.88	5.70	5.93	9.50	9.45	13.27	13.52	14.50	14.29	*c*	3.25 (20)
CoTIB-*N*-*tert*-Bu	59.57	59.13	6.36	6.80	6.31	6.15	13.29	13.00	14.46	14.29	0.90	4.44 (20)
CoTIB-DPT	56.06	56.70	5.41	5.56	9.80	9.82					0.98	4.10 (22)
CoTIB-MeDPT	57.00	57.15	5.69	5.94	9.50	9.60	13.32	13.00	14.49	14.40	*c*	4.17 (20)

[a] Ratio of the found to the theoretical molecular weight for *ca.* 10^{-2} *M* solutions in 1,2-dichloroethane at 37°. [b] This compound was first reported in ref 4. [c] The compound decomposes upon standing in solution.

Some TIB derivatives has been previously reported.[4]

The aim of this research is to compare the complexing ability of SAL and TIB ligands with respect to the stereochemistry and to the tendency of the obtained complexes to give rise to conformational equilibria in solution.

Experimental Section

The *o*-mercaptolbenzaldehyde (TIB) was obtained in solution of diethyl ether from *o*-mercaptolbenzoic acid as described elsewhere.[5] The concentration of the aldehyde in solution was determined by weighing the 2,4-dinitrophenylhydrazone derivative. The Schiff base ligands were obtained by adding the stoichiometric amount of amine (or polyamine) in absolute alcohol to a measured volume of the TIB solution in an ice bath. After 30 min the solution was concentrated under vacuum to remove the ether and again diluted with alcohol to obtain *ca.* 20 ml of 10^{-1} *M* solution. By adding the stoichiometric amount of metal acetate (in water or absolute alcohol depending on whether the ligand contains mono- or polyamines) to the Schiff base solution, upon standing, crystals were obtained. The cobalt complexes were prepared under nitrogen. The complexes were recrystallized from a mixture of chloroform and petroleum ether (bp 40–70°).

The NiTIB-DPT and NiTIB-MeDPT complexes add a molecule of chloroform by recrystallization which is lost by heating at 60° under vacuum.

Spectrophotometric, magnetic, and molecular weight measurements were performed with the apparatus and techniques previously described.[6] The pmr spectra were recorded with a Varian DA-60-IL spectrometer operating at 60 Mcps and 26° (except when otherwise specified).

Results

The complexes prepared are listed in Table I along with their elemental analysis, experimental molecular weights, and magnetic properties. All of the complexes are monomeric in 1,2-dichloroethane solution and their solution and reflectance spectra are substantially identical. Therefore the diamagnetic complexes, which have four potential donor atoms, have to be planar. Their electronic spectra, in fact, show only one peak or shoulder at ≃15 kK and, of course, charge-transfer bands above this value.[7]

The paramagnetic NiTIB-*N*-*tert*-Bu complex is presumably pseudotetrahedral, as it is isomorphous with the analogous cobalt complex and its spectrum is correlatable with that of the pseudotetrahedral NiSAL-*N*-*tert*-Bu complex[8] (see Figure 1).

The nickel and cobalt complexes with the pentadentate ligands (R = H, R = Me) are isomorphous. Since they are monomeric and paramagnetic and their electronic spectra correspond to those of the analogous

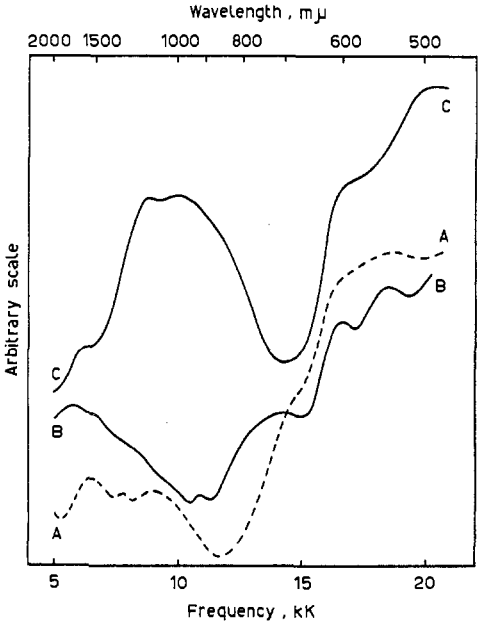

Figure 1.—Diffuse reflectance spectra: A, NiTIB-*N*-*tert*-Bu; B, NiSAL-*N*-*tert*-Bu; C, CoTIB-*N*-*tert*-Bu.

SAL complexes[9] (Figure 2), for which five-coordination was ascertained by X-ray analysis,[10] we assign them a five-coordinate structure.

Discussion

For comparison purposes we are reminded that bis(*N*-alkylsalicylaldiminato)nickel(II) complexes give rise in solution to temperature-dependent equilibria between polymeric six-coordinated, monomeric planar, and monomeric tetrahedral species.[1,2] Such an equilibrium moves to the right as the substitution on the α carbon of the amine increases; *i.e.*, the α carbon is primary, secondary, or tertiary. For example the NiSAL-*N*-Et complex, planar in the solid state, gives

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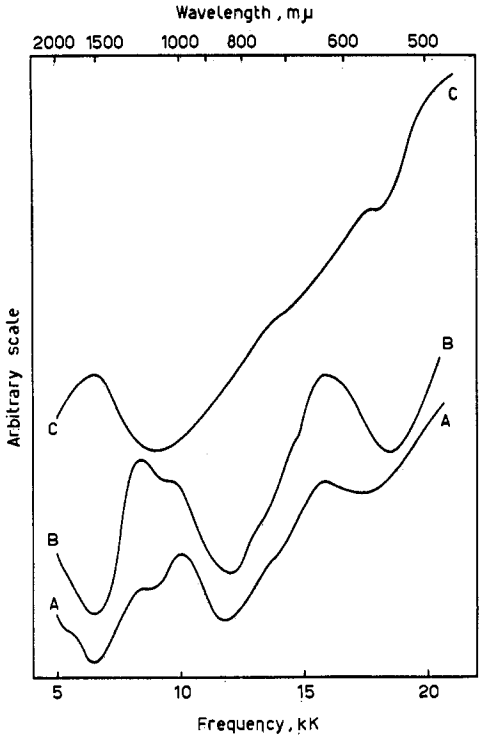

Figure 2.—Diffuse reflectance spectra: A, NiTIB-MeDPT; B, NiSAL-MeDPT; C, CoTIB-MeDPT.

rise to a percentage of six-coordinated associate forms in solution.[11] Tetrahedral species may be obtained only at high temperatures in the melted state.[12] The SAL-*i*-Pr derivative, pseudotetrahedral in the solid state (μ_{eff} = 3.3 BM),[13] gives rise to a planar–tetrahedral equilibrium in solution[8] whereas associated pseudooctahedral species occur at low temperatures.[8,11] The NiSAL-*N*-*tert*-Bu complex is fully tetrahedral under any circumstance.[8]

In contrast with this behavior, the Ni^{II}–TIB complexes with normal or α secondary alkyl groups are planar both in the solid state and in solution, and, again in contrast with the SAL complexes,[2] the TIB derivatives do not add pyridine to form six-coordinated complexes. Only with the most bulky *tert*-butyl group is a pseudotetrahedral stereochemistry obtained. Therefore it can be concluded that the sulfur atoms in this type of ligands strongly stabilize the planar stereochemistry with respect to the tetrahedral or the octahedral one. This agrees with the previous results obtained by Holm, *et al.*, with bis(β-keto amine)- and bis(β-amino thione)nickel(II) complexes.[14]

Pmr Spectra.—The pmr spectra of some nickel complexes have been recorded and their spectra are shown in Figure 3. Peak assignment has been obtained from comparison with the analogous SAL derivatives[15,16] (see spectrum C of Figure 3) and from shift temperature dependence. The pseudotetrahedral complex shows a spectrum similar to that of the analogous SAL derivative except for the H-6 signal which is more downfield for the TIB complex (−6.8 ppm against −3.8 ppm of isotropic shift) and therefore proton shift alternation is qualitatively better. The fact that the H-6 position is the most sensitive to dipolar shift contributions in this type of complexes and its contact shift is expected to be of the same order of magnitude of that of H-4[17] indicates that the TIB complex is fairly magnetically isotropic with respect to the tetrahedral SAL complexes.[18]

In the case of five-coordinate complexes the difference between SAL and TIB complexes is more marked. The former complexes show two peaks for each aromatic proton at every temperature.[16] The structure of the SAL-MeDPT complex,[10] reported in Figure 4, is intermediate between a trigonal bipyramid and a tetragonal pyramid with the N_3–Ni–N angles of $\simeq$90°. The N_3–Ni–O angles, however, are inequivalent being 113 and 106°. This inequivalence, in absence of diastereoisomers, was thought[16] to be the cause of the signal splitting. However, if this were the case, one would expect four signals for each aromatic proton in that the structure revealed two geometrical isomers:[10] one with the R group pointing at the salicylaldimine ring forming an N_3–Ni–O angle of 106° and the other with the R group pointing at the other salicylaldimine group.

The spectra of the NiSAL-MeDPT complexes, showing two signals for each aromatic proton but only one signal for the NCH_3 group,[16] are consistent with a solution structure having equal N_3–Ni–O angles. The small difference observed in these two angles in the solid structure can well be due to solid-state effects. Furthermore such a difference should not be detected by pmr in solution because the two angles will be averaged through a rapid rocking of the angles. Inequivalence of the two salicylaldimine moieties arises therefore from the lack of a plane of symmetry or a C_2 axis because of the presence of the R group. Just as for the similar case of tetrahedral $Ni(B_2pn)X_2$ complexes,[19] this type of nonequivalence is markedly detected by pmr.

The signal-splitting variation with the solvent and the non-Curie behavior of these splittings observed for the NiSAL-MeDPT complex may be attributed to small changes in the N_3–Ni–O angles toward 120° (trigonal-bipyramidal structure) or 90° (square-pyramidal structure).

In the case of the NiTIB-DPT complex only one signal for each set of ligand protons is observed at a temperature >20° (Figure 2B). For the H-4 and H-6 signals a first-order spin–spin coupling (J = 7 cps) is observed. Between +10 and −15° the spectrum shows very broad signals and plateaus. This is typical of systems containing two or more forms in equilibrium interconverting in a time of the same order of magnitude of pmr scale.[20] Below −25° two signals for each aromatic proton and three (of intensity 1:1:2) for the β-CH_2 groups are observed (Figure 3D). Since no

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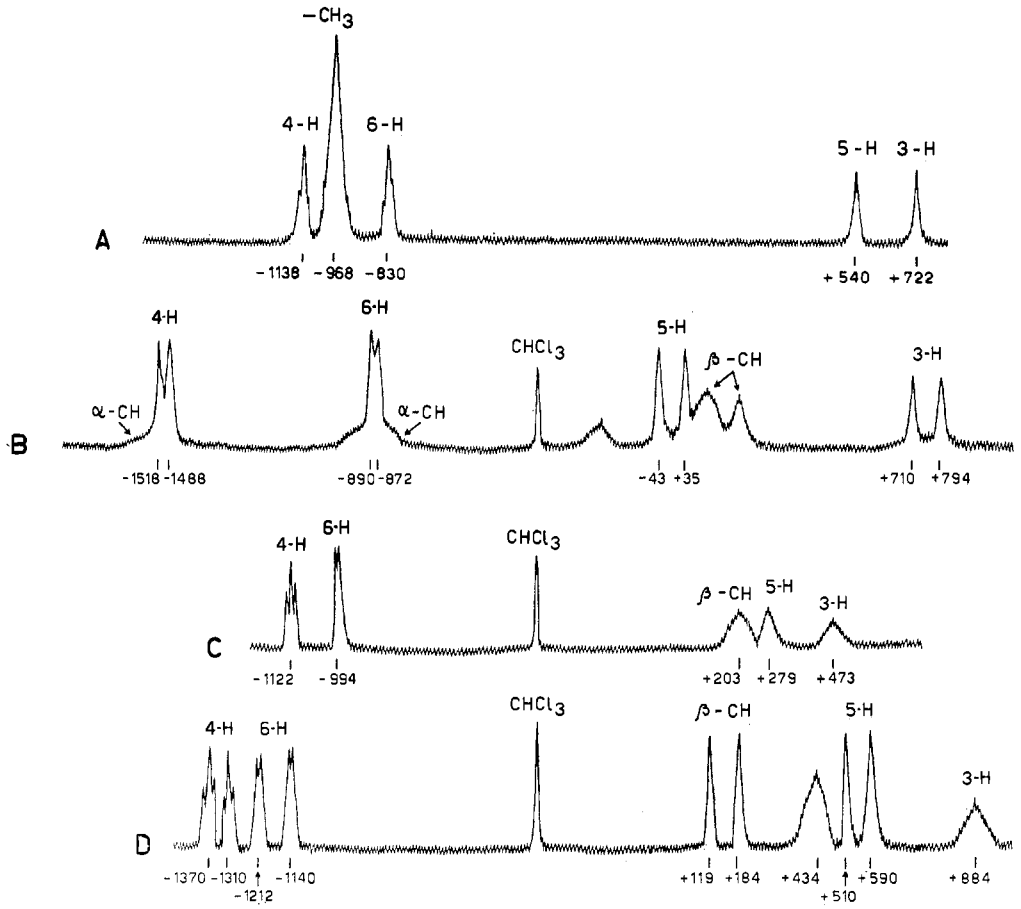

Figure 3.—Proton magnetic resonance spectra: A, NiTIB-*N-tert*-Bu in CD_2Cl_2; B, NiSAL-MeDPT in $CDCl_3$ (taken from ref 15); C and D, NiTIB-DPT in $CDCl_3$ at +26 and at −47°, respectively. The proton chemical shifts are given in cps from internal TMS (at 60 Mcps).

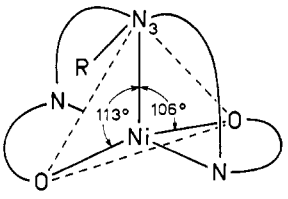

Figure 4.—Scheme of the X-ray structure of NiSAL-MeDPT.

splitting of the aromatic proton resonances is observed, the two aromatic groups are equivalent at room temperature. Assuming a structure of the type of Figure 4, this equivalence may be achieved through a rapid exchange of positions between the two aromatic moieties in such a way that both of them "see" equally the N–H group. This equilibrium may occur through the detachment of the two sulfur atoms, the exchange of their positions (which involves a rearrangement of the methylenic chains but leaves unaltered the N–H group), and following restoration of the Ni–S bonds. Below −25° such interconversion could be slow on pmr scale time so that the two aromatic moieties become nonequivalent and a splitting of the peaks is observed.

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