and interact less strongly with the ligand antibonding orbitals. However, on passing from Fe(III) to Co(II), the addition of a positive nuclear charge is accompanied by the addition of two electrons. It is not implausible that the additional shielding of two electrons will more than compensate for one unit of nuclear charge so that the shift for Co(II) is rather greater than that for Fe(III) and is, in fact, quite close to that for Mn(III).

There are some clear parallels between the interactions discussed above and the chemistry of the transition metal ions. Thus, the ease of electron transfer from metal to ligand is clearly related to the ease of oxidation of the ion to the next highest valence state and that of transfer from ligand to metal to the ease of reduction to the next lowest valency. In the series Ti(III), V(III), and Cr(III), there is a sharp decline in the ease of oxidation in accord with the decreased spin delocalization in the antibonding orbital indicated by the contact shifts. In the group VI elements, Mo(III) is much more easily oxidized than Cr(III) and this again is reflected in the larger shifts observed. On passing to the series Cr(III), Mn(III), Fe(III), reduction to the lower valency becomes an important consideration and this is accompanied by significant contact shifts arising from ligand-to-metal charge transfer. If the Co(II) shifts are indeed predominantly contact, the process must be one of metal-to-ligand transfer as might have been anticipated from the existence of very stable Co(III) complexes. The Ni(II) compound on the other hand does not show this behavior and this can be correlated with the relative instability of Ni(III).

In conclusion, there is now perhaps sufficient data available from this work and previous studies on the n.m.r. of paramagnetic transition metal complexes to allow some tentative generalizations to be made regarding the interpretations of the observed shifts.

1. In the first transition series, providing the complexes are of fairly high symmetry, pseudo-contact effects do not seem to be very important. In the second transition series they become more significant, and in rare earth complexes they probably dominate.

2. For a given ligand and different metal ions, interactions with both bonding and antibonding ligand $\pi$-orbitals can occur. A qualitative prediction of which will be the more important can probably be made in many cases by consideration of the ease of reduction to the lower valency or of oxidation to a higher valency.

3. For a given metal ion and different ligands the crucial factor is the energy separation between the metal d-orbitals and the various ligand molecular orbitals. This is illustrated by data given in Table V comparing calculated energy levels for the aminotropone-imine and acetylacetonate ions. In the former case there is a bonding orbital of rather high energy and in accordance with this, ligand-to-metal spin transfer seems to dominate most of the aminotroponeimineates so far examined.[26] In the latter case both the top bonding and the bottom antibonding orbital are lower in energy and as discussed above metal-to-ligand charge transfer must also be considered. The possibility also remains that a $\sigma$-orbital may be the most favorably situated and this is perhaps the case for ligands such as pyridine[25] and amino acids.[27] A simple MO calculation, using Hoffman's[28] extended Hückel treatment if $\sigma$-orbitals are also to be considered, would be sufficient to make a qualitative prediction about the behavior of a given ligand. The extent of the applicability of these generalizations can only be determined when more detailed and extensive experimental results become available.

(26) Reference 1 and D. R. Eaton, W. R. McClellan, and J. F. Weiher, unpublished results.
(27) C. C. McDonald and W. D. Phillips, *J. Am. Chem. Soc.*, 85, 3736 (1963).
(28) R. Hoffman, *J. Chem. Phys.*, 39, 1397 (1963).

# Structure Mimicry in Solid Solutions of 3d Metal Complexes with N-Methylsalicylaldimine (Msal-Me)

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*The complex bis(N-methylsalicylaldiminato)zinc(II) (Zn-sal-Me) is a pentacoordinate dimer. The complexes Cosal-Me and Mnsal-Me are isostructural with the Znsal-Me complex. Each of the former forms a binary solid solution with the latter when recrystallized at room temperature from common organic solvents. The diamagnetic complex Nisal-Me (forms α and β), although planar, also forms binary solid solutions with Znsal-Me. In a solid solution rich in the latter compound, Nisal-Me assumes the molecular and crystalline structure of the zinc complex and becomes pentacoordinate and paramagnetic. Addition of Znsal-Me to a Nisal-Me-rich organic solution, followed by crystallization, results in the formation of a solid solution which has the structure of the γ form of Nisal-Me. This form is paramagnetic and probably polymeric. It is normally obtained by heating crystalline diamagnetic Nisal-Me above 180°. In this solid solution, Znsal-Me transforms to the molecular and crystalline structure of γ-Nisal-Me which may be considered as the host lattice in this case. Analogous structural mimicry is demonstrated also by Cusal-Me with Znsal-Me. Cosal-Me in benzene or chloroform transforms partially to the monomeric tetrahedral form.*

## Introduction

The ability to form solid solutions has generally been used as a criterion of isomorphism for metallic complexes. We have observed that several bis(N-methyl-salicylaldiminato)metal(II) complexes (Msal-Me) form binary solid solutions even when their *molecular* and crystalline structures differ. In these cases the complex which is present as the solute (guest) assumes the *molecular* and crystalline structure of the complex which is in excess (host). Only recently one analogous case has been reported.[1] We suggest to name this phenomenon "structure mimicry." In this paper we report the results of a systematic study of complexes in the series Msal-Me with particular emphasis on their stereochemistry and the structure of various such binary solid solutions. These systems were studied by X-ray crystallography, spectrophotometry, and magnetochemistry.

## Experimental

*Preparation of the Compounds.* The compounds of N-methylsalicylaldimine with nickel(II)[2] and copper(II)[3] have been prepared as previously described. The zinc(II) complex was described by Charles,[4] but we have found the following method more suitable.

*Bis(N-methylsalicylaldiminato)zinc(II).* A saturated aqueous solution of 0.10 mole of zinc acetate was added to a solution of 0.20 mole of salicylaldehyde and 0.30 mole of methylamine in 100 ml. of ethanol. The mixture was refluxed for 0.5 hr.; on cooling, pale straw-colored crystals separated which were recrystallized twice from chloroform (m.p. 260–262°). This compound is sparingly soluble in chloroform (*ca.* 0.05 *M* at room temperature).

*Anal.* Calcd. for $C_{16}H_{16}N_2O_2Zn$: N, 8.4; Zn, 19.6. Found: N, 8.3; Zn, 19.4.

The complexes of manganese(II) and cobalt(II) were prepared and collected under a nitrogen atmosphere in order to avoid oxidation by atmospheric oxygen. In the crystalline state both these complexes are fairly stable to air, while in solution they are readily oxidized. The cobalt(II) compound has been already described.[5]

*Bis(N-methylsalicylaldiminato)cobalt(II).* A concentrated aqueous solution of 0.01 mole of cobalt acetate was added to a warm solution of 0.02 mole of salicylaldehyde and 0.03 mole of methylamine in 40 ml. of ethanol. After a few minutes deep green crystals began to separate from the red solution. When crystallization was complete, the crystals were collected on a filter, washed with petroleum ether, and dried (m.p. 231–234°).

*Anal.* Calcd. for $C_{16}H_{16}N_2O_2Co$: N, 8.6; Co, 18.0. Found: N, 8.7; Co, 18.6.

*Bis(N-methylsalicylaldiminato)manganese(II).* The same procedure used for the cobalt complex was employed. The precipitation of crystals was accomplished

by adding 50 ml. of hot water. On cooling orange crystals separated (m.p. 305–307°).

*Anal.* Calcd. for $C_{16}H_{16}N_2O_2Mn$: N, 8.6; Mn, 16.9. Found: N, 8.6; Mn, 16.9.

Attempts to prepare the analogous ferrous compound led to the formation of a red crystalline product which readily decomposed in air becoming black even when dry.

*Solid Solutions.* The solid solutions of the Msal-Me complexes were obtained by evaporating the mixed chloroform solutions of the components. The resulting crystals were collected on a filter, washed with chloroform and petroleum ether, and then dried *in vacuo.* The powders corresponding to the phase A of the Nisal-Me–Znsal-Me system, which are insoluble in chloroform, were refluxed in chloroform for about 10 min.; then they were collected and washed several times with chloroform and petroleum ether. Both the nitrogen and metal contents in all these products have been determined. The nickel or copper content was determined spectrophotometrically by measuring the optical densities of the solutions in pyridine. From the values of the molar absorbances in pyridine of Nisal-Me ($\epsilon_{950m\mu}$ 15.2), Cusal-Me ($\epsilon_{650m\mu}$ 108), and Znsal-Me ($\epsilon_{950m\mu}$ 0.07; $\epsilon_{650m\mu}$ 0.14), the percentage of nickel or copper complex was calculated. This procedure was previously checked by determining the nickel or copper content by means of the dimethylglyoxime or iodometric method, respectively.

*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 with freshly distilled water and Co[Hg(CNS)₄].[7] The molar diamagnetic corrections for all these complexes were assumed to be $-167 \times 10^{-6}$ c.g.s. unit; *i.e.,* the experimentally found value for the Znsal-Me complex. The gram susceptibilities of nickel(II) and copper(II) complexes contained in the solid solutions with Znsal-Me were calculated from the values of the gram susceptibilities of the solid solutions by using the mixture law. The values of gram susceptibilities so obtained are estimated to be accurate to within 2%.

*Spectrophotometric Measurements.* The absorption spectra were recorded with a Beckman DK2 spectrophotometer equipped with a thermostated cell housing. The solutions of the cobalt(II) complex were prepared and transferred to the cell in an atmosphere of pure nitrogen. The reflectance spectra were measured using the standard Beckman reflectance attachment and magnesium oxide as the reference.

## Results and Discussion

The complex Nisal-Me has been extensively studied as the first example of "magnetically anomalous" nickel(II) complexes.[8,9] Three crystalline forms of this compound are known to exist. The $\alpha$-ortho-rhombic[10] and $\beta$-monoclinic[11] forms are those usually

(1) A. Chakravorty, *Inorg. Chem.*, **4**, 127 (1965).
(2) W. Klemm and K. H. Raddatz, *Z. anorg. allgem. Chem.*, **250**, 207 (1943).
(3) L. Sacconi, M. Ciampolini, F. Maggio, and G. Del Re, *J. Am. Chem. Soc.*, **82**, 815 (1960).
(4) R. G. Charles, *J. Inorg. Nucl. Chem.*, **9**, 145 (1959).
(5) H. Nishikawa, S. Yamada, and R. Tsuchida, *Z. anorg. allgem. Chem.*, **316**, 278 (1962).

(6) L. Sacconi, M. Ciampolini, F. Maggio, and F. P. Cavasino, *J. Inorg. Nucl. Chem.*, **19**, 73 (1961).
(7) *Cf.* B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p. 415.
(8) *Cf.* J. R. Miller, *Advan. Inorg. Chem. Radiochem.*, **4**, 159 (1962).
(9) L. Sacconi, *Experientia Suppl.*, **9**, 148 (1964).
(10) J. Ferguson, *J. Chem. Phys.*, **34**, 611 (1961).

obtained by crystallization from organic solvents. They are diamagnetic, with planar nickel, as shown by X-ray structure determination.[11,12] The γ-form is obtained by heating diamagnetic Nisal-Me above 180°.[13] This high-temperature form is paramagnetic with $\mu_{eff}$ = 3.4 B.M.[13] and is a yellow-green violet microcrystalline powder. It is insoluble in all inert solvents, and this can be attributed to its polymeric structure.[13,14] Single crystals cannot be isolated and this has prevented X-ray structural identification.

The complex Cusal-Me exists in three crystalline modifications[15]: α and γ, both orthorhombic, and β, which is monoclinic. The forms α and β are isomorphous with the corresponding form of Nisal-Me. The copper has a planar coordination geometry.[16]

The complex Znsal-Me exists in a light straw-colored, triclinic form. A complete three-dimensional X-ray analysis carried out in this laboratory has shown that this complex exists as a dimer in the solid state.[17] Each atom of zinc, bound to two atoms of oxygen and two atoms of nitrogen, has a coordination of five *via* sharing with an oxygen atom from a neighboring molecule. The ligand donor atoms are situated at the vertices of two trigonal bipyramids with a common edge. The zinc atoms are at the centers of the bipyramids according to the following sketch.
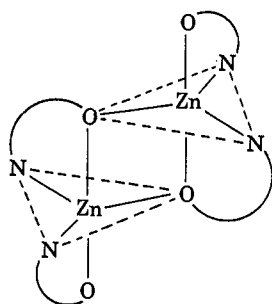


The same structure must also be attributed to the complexes of manganese(II) and cobalt(II) with N-methylsalicylaldimine. Indeed, X-ray measurements on single crystals have shown that both the complexes Mnsal-Me and Cosal-Me are isostructural with the complex Znsal-Me.[17]

The complex Cosal-Me is in the form of triclinic emerald-green crystals. The magnetic moment of cobalt(II) is 4.62 B.M. at room temperature and decreases with decreasing temperature. The magnetic susceptibility follows the Curie–Weiss law with a value of $\theta$ = +24° (Table I). This complex represents thus the first example of pentacovalent high-spin cobalt(II) whose structure has been established by X-ray analysis.[18] Its reflectance spectrum shows four bands with

peaks at 5600, 11,400, 15,200, and 19,600 cm.[−1] (Figure 1). It differs considerably from that of other high-spin complexes of cobalt(II) with N-substituted salicylaldimines existing in tetrahedral configuration (three bands at *ca.* 8000, 12,000, and 17,500 cm.[−1])[19] or in octahedral symmetry following the addition of two molecules of pyridine (two bands at 10,000 and 17,800 cm.[−1]).[19]

The complex Mnsal-Me exists as orange crystals with a magnetic moment of 5.95 B.M. (Table I). This pentacoordinate complex of manganese(II) is believed to be the first of its kind described to date.

*Binary Solid Solutions of Complexes Msal-Me.* Evaporation of the solvent chloroform from binary solutions of these complexes of manganese, cobalt, and zinc results in the formation of solid solutions with X-ray powder patterns identical with those of pure solid complexes. Therefore, their structure is also identical as was anticipated. Interesting phenomena were observed when partial evaporation instead was carried out on chloroform solutions containing Znsal-Me and Nisal-Me or Znsal-Me and Cusal-Me. Differing systems may be obtained, depending upon the relative proportions of the two components.

*System Nisal-Me–Znsal-Me. Phase A.* When the ratio by weight between the quantities of Nisal-Me and Znsal-Me is greater than 30:70 a gray-green precipitate of violet shade separates from solution. The color is similar to that of the γ-form of Nisal-Me. Just as with the latter compound, this precipitate is insoluble in chloroform and all other inert solvents. It consists of Nisal-Me and Znsal-Me with a weight per cent of the former ranging approximately between 50 and 80%. The nickel(II) in this precipitate has a magnetic moment of *ca.* 3.1 B.M. (Table I). In the X-ray powder diagrams, only the lines of the γ-form of Nisal-Me are present. It is thus evident that these solids are homogeneous with the same lattice and molecular structure as the γ-form of Nisal-Me. Reflectance spectra provide additional and independent evidence for the identity of molecular structures. Their spectra, taken from 6000 to 20,000 cm.[−1] (Figure 2), show that they are essentially identical with the spectra of γ-Nisal-Me (Znsal-Me is transparent beyond 22,000 cm.[−1]). We therefore conclude that the presence of Znsal-Me induces the complex Nisal-Me to assume its γ-form structure even at room temperature. Simultaneously, the guest complex Znsal-Me within the host lattice assumes the configuration of the γ-form of Nisal-Me. Thus the guest complex imitates the lattice structure of its host. We propose to designate this phenomenon by the term "structure mimicry (or mimesis)." This term designates the cocrystallization of such a binary pair with the simultaneous change in the *molecular* and crystal structure of the guest complex to that of the host.

*The System Nisal-Me–Znsal-Me. Phase B.* When the weight ratio of Nisal-Me to Znsal-Me in chloroform is less than *ca.* 30:70, triclinic yellow-green crystals are obtained. The crystalline habit and the powder X-ray diagram are identical with those

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

(12) *Cf.* ref. 10.

(13) L. Sacconi, P. Paoletti, and R. Cini, *J. Inorg. Nucl. Chem.*, **8**, 492 (1958); *J. Am. Chem. Soc.*, **80**, 3583 (1958).

(14) C. M. Harris, S. L. Lenzer, and R. L. Martin, *Australian J. Chem.*, **11**, 33 (1958).

(15) *Cf.* ref. 8, p. 159.

(16) B. Meuthen and M. von Stackelberg, *Z. anorg. allgem. Chem.*, **305**, 279 (1960); E. C. Lingafelter, B. Morosin, and G. L. Simmons, *Acta Cryst.*, **13**, 1025 (1960).

(17) P. L. Orioli, L. Sacconi, and M. Di Vaira, *Chem. Commun.* (London), **1**, 103 (1965).

(18) *Cf.* A. F. Wells, "Structural Inorganic Chemistry," Oxford University Press, London, 1962, pp. 918, 919. A pentacoordinate adduct of bis(N-2,6-dimethylphenylsalicylaldiminato)cobalt(II) with one

molecule of pyridine has been isolated by Professor S. Yamada (private communication).

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

Table I. Magnetic Data for Msal-Me Complexes and Their Solid Solutions

| Compound or system | Composition, % | Temp., °C. | $\chi_g \times 10^6$ | $\chi_{M^{2+}} \times 10^{6a}$ | $\mu_{eff}$, B.M. |
|---|---|---|---|---|---|
| Mnsal-Me | | 14 | 46.50 | 15,300 | 5.95 |
| Cosal-Me | | −194 | 82.70 | 27,300 | 4.17 |
| | | −89 | 40.80 | 13,500 | 4.47 |
| | | 18 | 27.20 | 9,100 | 4.62 |
| Znsal-Me | | 12 | −0.50 | Diamagnetic | |
| Nisal-Me–Znsal-Me | | | | | |
| Phase A | Nisal-Me, 77 | 21 | 9.55 | 4,250 | 3.2 |
| | 70 | 21 | 8.55 | 4,200 | 3.2 |
| | 66 | 21 | 7.65 | 4,050 | 3.1 |
| | 51 | 22 | 6.10 | 4,250 | 3.2 |
| | 49 | 23 | 5.45 | 4,000 | 3.1 |
| Phase B | 8.3 | 21 | 0.58 | 4,200 | 3.2 |
| | 4.8 | 22 | 0.09 | 4,000 | 3.1 |
| | 3.3 | 21 | −0.05 | 4,400 | 3.2 |
| Cusal-Me–Znsal-Me | | | | | |
| | Cusal-Me, 14.6 | 25 | 0.25 | 1,720 | 2.0 |
| | 11.9 | 25 | 0.15 | 1,790 | 2.0 |
| | 8.5 | 25 | −0.07 | 1,700 | 2.0 |

[a] $M^{2+}$ means a paramagnetic ion: $Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}$.

of Znsal-Me. Thus, these are solid solutions in which the component molecule Nisal-Me substitutes into the lattice of Znsal-Me assuming the structure of the

11,800, and 20,400 cm.$^{-1}$ (Figure 2). This spectrum differs from those of other complexes of high-spin nickel(II) with salicylaldimine and tetrahedral or
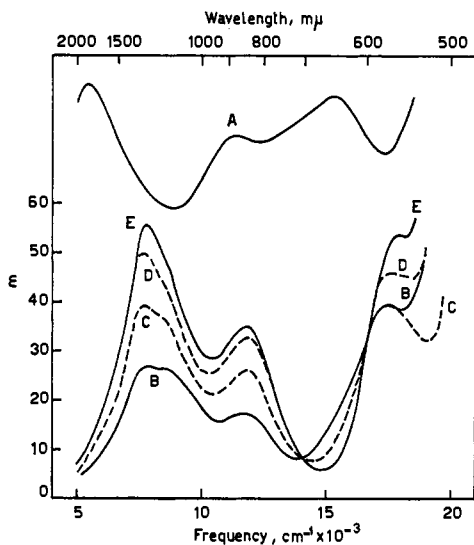


Figure 1. Spectra of Cosal-Me: A, by reflectance (absorption scale arbitrary); B and C, in benzene at 20°, 16 and 8 m$M$, respectively; D, 8 m$M$ in benzene at 60°; E, 33 m$M$ in chloroform at 20°.
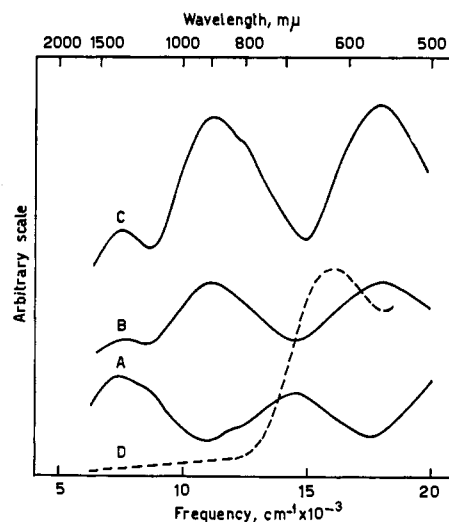


Figure 2. Reflectance spectra of solid solutions of Nisal-Me–Znsal-Me: phase B, 8% Nisal-Me (curve A), and phase A, 50% Nisal-Me (curve B). Reflectance spectra of Nisal-Me: paramagnetic polymeric γ-form (curve C) and diamagnetic planar β-form (curve D).

latter. Therefore, each atom of nickel(II) is situated in the center of a trigonal bipyramid. This type of substitution takes place up to ca. 10% by weight.

The magnetic moment of nickel(II) in these solid solutions is 3.1–3.2 B.M. (Table I). We believe that this represents the first known complex of high-spin pentacoordinate nickel(II) in a trigonal bipyramid. An additional complex of high-spin pentacoordinate nickel(II), but with a distorted square-pyramidal coordination geometry, has recently been isolated in this laboratory.[20]

Reflectance spectra of these solid solutions of Nisal-Me in Znsal-Me show two bands with peaks at 7300 and 14,400 cm.$^{-1}$ and with shoulders at 9100,

octahedral structures.[21] This therefore constitutes a proof that the nickel(II) in these solid solutions does not have any of the above coordination geometries. Its spectrum differs also from that of the γ-form of Nisal-Me. This spectrum may be considered as that of nickel(II) in a triplet state, pentacoordinated and in the center of a distorted bipyramid.

The System Cusal-Me and Znsal-Me. Homogeneous salad-green crystals are obtained following the evaporation of chloroform containing Cusal-Me (olive-green in color) and Znsal-Me. Their crystal habits and powder patterns are identical with those of pure Znsal-Me.

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

(21) L. Sacconi, P. L. Orioli, P. Paoletti, and M. Ciampolini, Proc. Chem. Soc., 253 (1962); L. Sacconi, P. Paoletti, and M. Ciampolini, J. Am. Chem. Soc., 85, 411 (1963).
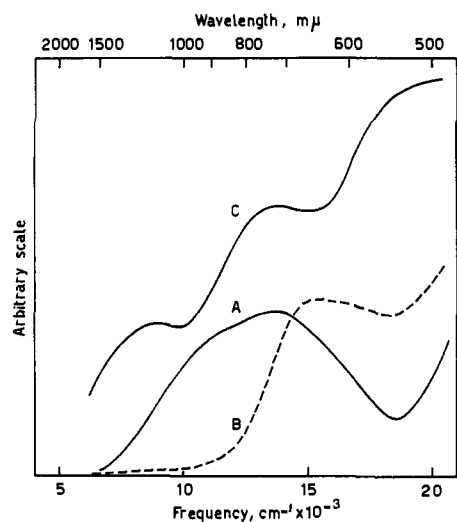
Figure 3. Reflectance spectra of the solid solution of Cusal-Me–Znsal-Me: 12% Cusal-Me (curve A), planar $\beta$-form of Cusal-Me (curve B), and tetrahedral bis(N-isopropylsalicylaldiminato)-copper(II) (curve C).

Thus, also the normally planar molecule Cusal-Me in solid solution assumes a stereochemistry equal to that of the host Znsal-Me. The copper atoms are therefore surrounded by five ligand atoms situated at the vertices of a trigonal bipyramid.

Magnetic susceptibility measurements in these solid solutions show that all the atoms of copper have the normally unpaired electron ($\mu_{eff}$ = $ca.$ 2.0 B.M., Table I). The reflectance spectrum of Cusal-Me in the host lattice of Znsal-Me shows a large band with a peak at 13,000 cm.$^{-1}$ and a shoulder at 11,000 cm.$^{-1}$ (Figure 3). This spectrum differs from those of planar or distorted tetrahedral bis(N-alkylsalicylaldiminato)-copper(II) complexes.[22]

The behavior of these complexes in the solid solutions shows that their molecular structures are very labile. Thus the difference in energies between the various possible structures of each complex is very small. The influence of the host lattice suffices to induce the guest complex to change its own structure in favor of that of the host complex. In a similar manner, when many metal complexes of N-alkylsalicylaldimines are dissolved, the solute–solvent interactions which replace the lattice forces assist in stereochemical transformations and conformational equilibria take place. Thus the nickel(II)[21,23] and copper(II)[22] complexes of N-alkylsalicylaldimines, which are planar or

(22) L. Sacconi and M. Ciampolini, *J. Chem. Soc.*, 276 (1964).
(23) L. Sacconi, *ibid.*, 4608 (1963).

tetrahedral in the solid state, in solutions of "inert" solvents give rise to equilibria between the two forms.

*Conformational Equilibrium of Cosal-Me in Solution.* Solutions of Cosal-Me in benzene are reddish brown in contrast to its solid state which is green. The absorption spectrum of the solutions shows bands at 7800, 11,800, and 12,500 cm.$^{-1}$, indicating the presence of the tetrahedral forms.[19] Nevertheless, the molar absorbance at the peaks, per gram-atom of cobalt, is strongly dependent on the concentration of the solution and on temperature (Figure 1, Table II). At concentration of $ca.$ $10^{-2}$ $M$, the absorbance is approximately one-half of that exhibited by other compounds of cobalt(II) with N-alkylsalicylaldimines monomeric in benzene.[19] This leads to the conclusion that a portion of the compound exists in solution in the tetrahedral form while the remaining part is probably present as the dimer. An increase of temperature of the solutions results in the simultaneous increase of the band height, *i.e.*, of the proportion of the monomeric form. Unfortunately, the low solubility and high tendency toward oxidation of Cosal-Me have precluded reproducible molecular weight determinations.

Table II. Spectral Data for Cosal-Me in Solution

| Solvent | Concn., mM | Temp., °C. | $\epsilon_{7800cm.^{-1}}$ | $\epsilon_{11,800cm.^{-1}}$ |
|---------|------------|------------|------------|------------|
| Benzene | 6 | 20 | 40 | 26 |
| | 8 | 20 | 38 | 25 |
| | 8 | 60 | 50 | 33 |
| | 12 | 20 | 34 | 22 |
| | 16 | 20 | 27 | 17 |
| Chloroform | 33 | 20 | 56 | 35 |

Also the solvent affects this equilibrium. Thus the molar absorbances in chloroform solutions of $ca.$ $10^{-1}$ $M$ reach approximately the values found for the tetrahedral complexes of cobalt(II) with salicylaldimines.[19] This solvent effect may perhaps be attributed to hydrogen bonds formed between the phenolic oxygens and chloroform. This prevents the association of complexes *via* oxygen bridging. In pyridine, the absorption spectrum of Cosal-Me shows bands at 10,300 ($\epsilon$ 10) and 17,800 cm.$^{-1}$ ($\epsilon$ 19). These values indicate that the tetrahedral forms and the dimers are not present in appreciable amounts and that instead octahedral adducts with two molecules of pyridine are formed.[19]