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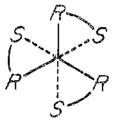
Isomerism in Complexes of Bidentate Meso Chelates

AIC404113

Sir:

The possibility of α, β (or facial, meridional) isomerism in octahedral complexes of unsymmetrical bidentate ligands is well known.[1] However, that a similar type of isomerism is possible in octahedral complexes of meso chelates, whose halves are distinguishable by their chirality (in the simplest case, *R* and *S*), has generally gone unrecognized.[2] Thus, recent papers[3,4] interpreting pmr spectra of Ni(*ms*-bn)$_3{}^{2+}$ (bn = 2,3-diaminobutane) have failed to consider the possible presence of two diastereomers—the *fac* isomer (**1**) with dissymmetric sites of only one chirality about each trigonal face and the *mer* isomer (**2**), obtained from **1** by switching a ligand end for end.



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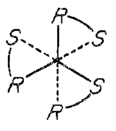

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The distinction between the two isomers is not a trivial one nor is their interconversion. Molecular models show a significant difference between the proton environments in *fac*- and *mer*-Ni(*ms*-bn)$_3{}^{2+}$. The *fac* isomer, apparently the only one considered to date in pmr spectral interpretations for these and similar complexes,[4,5] has C_3 symmetry (ignoring ligand conformation) and contains two magnetically nonequivalent sets of three methyl groups (or methine protons) each. The nonequivalence of the two methyl groups of a chelate in *fac*-Ni(*ms*-bn)$_3{}^{2+}$ is easily explained since the *R* and *S* dissymmetric centers must be chemically distinct in the overall Δ or Λ dissymmetry of the complex. In the *mer* isomer (C_1 symmetry), all methyl groups and all methine protons are magnetically nonequivalent.

Though the room-temperature pmr spectrum of Ni(*ms*-bn)$_3{}^{2+}$ solutions can be interpreted assuming only the presence of the *fac* isomer, the extreme broadness reported for the spectral peaks may indicate a mixture of *fac* and *mer*.[4] Molecular models indicate slightly more favorable nonbonded contacts in *fac*-Ni(*ms*-bn)$_3{}^{2+}$; however, the *mer* isomer has a statistical entropy contribution of $R \ln 3$ to its stability.[6] Thus the temperature-dependent pmr studies reported[4] for Ni(*ms*-bn)$_3{}^{2+}$ may, in fact, be affected by the presence of a temperature-dependent diastereomer equilibrium.

In their pioneering paper on ligand conformation,[7] Corey and Bailar, likewise, failed to notice the unique symmetry properties of meso chelates when they started that "even though α, β isomerism does not exist, there are 20 possible isomers of the ion [Co(stien)$_3$]$^{3+}$" (stien = stilbenediamine). Isomer enumeration by literature methods[8,9] for a system of *RR*, *SS*, and *RS* tris chelates shows that there are actually 32 isomers possible. Neglecting Δ, Λ isomerism, there are two structures each for the complexes Co(*ms*-stien)$_3{}^{3+}$ and Co(*d*-stien)(*l*-stien)(*ms*-stien)$^{3+}$ and three structures each for the complexes Co(*d*-stien)(*ms*-stien)$_2{}^{3+}$ and Co(*l*-stien)(*ms*-stien)$_2{}^{3+}$.

Isomers similar to those discussed above for an octahedral geometry are also possible for square-planar and tetragonal systems, where chelate ends of the same chirality may be either cis or trans. The presence of such isomers may explain some of the variations observed in (*ms*-stien)$_2$Ni^{II} and related complexes.[10,11] Appleton and Hall have recently proposed cis–trans structures for two isomers of square-planar bis(*meso*-pentane-2,4-diamine)platinum(II).[12]

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Single Ground State in the Oxygen-Inactive Form of *N*,*N*'-Ethylenebis(salicylideniminato)cobalt(II)

AIC404721

Sir:

The crystal and molecular structure of the oxygen-inactive form of *N*,*N*'-ethylenebis(salicylideniminato)cobalt(II), [Co(salen)]$_2$, has been determined.[1,2] The X-ray analyses show the cobalt to be five-coordinate with a square pyramidal arrangement of ligand molecules. The molecules are dimeric with out-of-plane bonds between the cobalt atoms and phenolic oxygen atoms as shown in Figure 1. The out-of-plane cobalt–oxygen distance is 2.259 Å.

Earlier investigators determined the high-temperature (90–400°K) dependent magnetic susceptibility for this compound, and the results are both interesting and controversial. In 1946 Calvin and Barkelew[3] measured the magnetic susceptibility over the temperature range 102–400°K by the Gouy method, and their rather extraordinary magnetic results are shown in Figure 2. Since no crystal transition had been observed for the compound over the temperature range investigated, Calvin and Barkelew attributed the unusual magnetic behavior to crystal field splitting caused by symmetry of rhombic or lower order. In 1959, with more sophisticated cryomagnetic equipment than that of Calvin and Barkelew, Figgis and Nyholm[4] measured the magnetic susceptibility over the range 90–300°K. For comparison, their results are also shown in Figure 2. The small curvature in the susceptibility–temperature curve was attributed to the presence of a small TIP term, of the order of 60 × 10^{-6} cgsu/mol, in the susceptibility. The two sets of data are in agreement at 300°K with each giving a magnetic moment of approximately 2.25 BM; however, the temperature dependence of each set is quite different. The limited temperature range over which these investigations were made and the nature of the magnetic data render the significance of their measurements doubtful. We have therefore measured the magnetic susceptibility over the temperature range of about 10–300°K and now report the true magnetic character of the compound. Our measurements were made using a Foner-type vibrating-sample magnetometer[5] operated at a field strength of 10,000 Oe and calibrated with a sample of very pure nickel metal and with $HgCo(NCS)_4$.[6] Temperature measurements were obtained with a precision germanium resistor and a high-impedance ac resistance bridge. The experimentally determined susceptibilities were corrected for the diamagnetism of the constituent atoms using Pascal's constants.[7]

The dramatic feature of our magnetic data is a pronounced maximum of the magnetic susceptibility near 34°K. This behavior indicates that the ground electronic state is of singlet multiplicity with a relatively small energy difference existing between this state and the paramagnetic triplet state. The temperature variation of the magnetic susceptibility is shown in Figure 3.

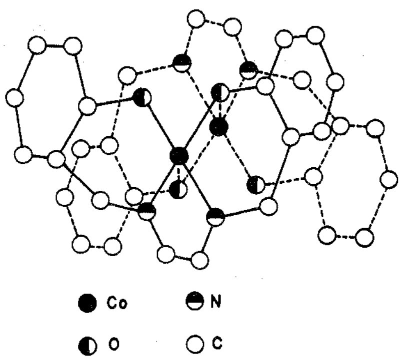

Figure 1. Schematic of the dimer [Co(salen)]$_2$.

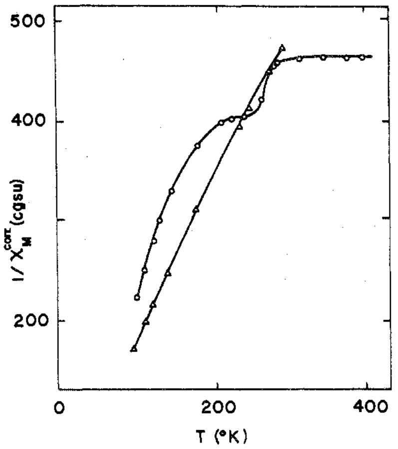

Figure 2. The magnetic results of Calvin and Barkelew (○) and of Figgis and Nyholm (△).

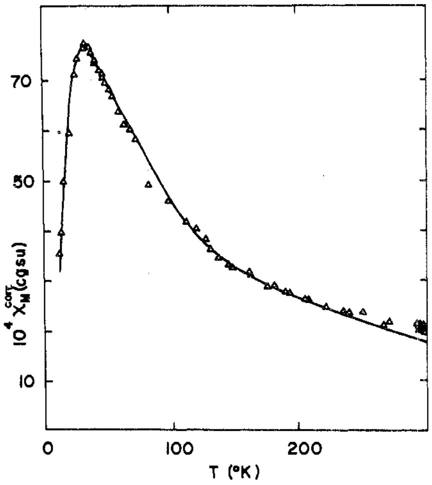

Figure 3. Plot of magnetic susceptibility *vs.* temperature for [Co(salen)]$_2$. The triangles represent the experimental data while the solid line represents the least-squares best fit to the Van Vleck equation.

With the assumption that these two electronic states (singlet ground state and low-lying triplet state) are sufficiently separated from other excited states such that the Van Vleck equation (eq 1)[8,9] applies, we have compared the data to the

$$\chi = [Ng^2\beta^2/3kT][1 + (1/3)\exp(-2J/kT)]^{-1} \qquad (1)$$

equation and find, from the best fit of experimental and calculated susceptibilities as determined by the minimum least-squares deviation, that $J = -20.0$ cm^{-1} and $g = 2.41$. As noted in Figure 3 the fit is very good; the average per cent deviation between the 52 experimental susceptibilities and those calculated using the best-fit parameters is only 2.7%. It is well known that effects such as spin–orbit coupling and crystal fields