(12) T. G. Appleton and J. R. Hall, *Inorg. Chem.*, 9, 1800 (1970).

Department of Chemistry
University of New Mexico
Albuquerque, New Mexico 87131

Robert E. Tapscott

Received June 25, 1974

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.

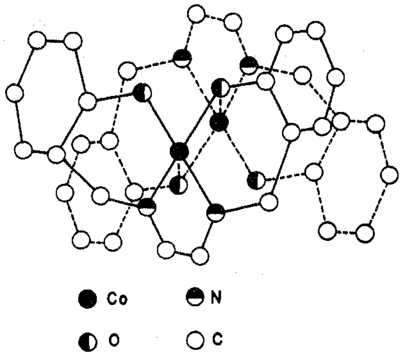

Figure 1. Schematic of the dimer [Co(salen)]$_2$.

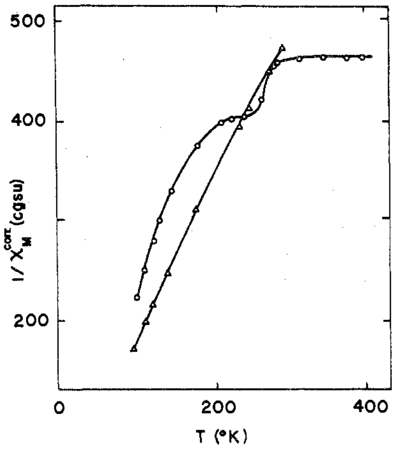

Figure 2. The magnetic results of Calvin and Barkelew (○) and of Figgis and Nyholm (△).

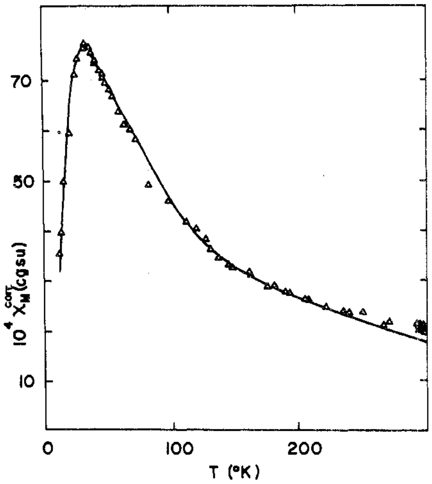

Figure 3. Plot of magnetic susceptibility *vs.* temperature for [Co(salen)]$_2$. The triangles represent the experimental data while the solid line represents the least-squares best fit to the Van Vleck equation.

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 may have important, though generally secondary, influences on the cooperative magnetic properties of substances. However these effects as well as vibrational partition functions are not needed in this case in order to obtain a good fit. It may be seen in Figure 3 that the experimental susceptibilities are slightly higher than those calculated in the temperature range 200–300°K. It is interesting to note that J varies within this range. If g is assumed to be constant and set equal to 2.41, J is found to be -15.2 cm^{-1} at 182°K and increases with temperature to $+43.8$ cm^{-1} at 297°K. Below 182°K where the fit is excellent J was found to be temperature independent. From 180 to 10°K the average value of J was calculated to be -20.9 cm^{-1} and the standard deviation from the average only 1.9 cm^{-1}. Ferromagnetic coupling between dimers may in part account for the high-temperature susceptibilities being slightly higher than theoretical. This effect would diminish at lower temperatures where the population of the triplet state would decrease.

Although a great number of dimeric copper(II) complexes have been shown to possess spin–spin coupling giving singlet ground states,[10] there have been, up to now, no well-documented examples of cobalt(II) dimers with singlet ground states. Previous work[3,4] which did not consider out-of-plane spin coupling must must be viewed in historical perspective. The unpaired electron of the Co^{2+} ion, with an idealized square-pyramidal ligand environment, is in the d_{z^2} orbital;[11] and, therefore, the exchange coupling is very likely a σ-orbital mechanism which is transmitted through the orbitals of the bridging oxygen atoms by electron transfer plus intraatomic direct exchange.[12]

Acknowledgment. The research conducted at West Texas State University was supported by the Robert A. Welch Foundation through Grant No. AE-491 and by Organized Research of West Texas State University. The work at the University of North Carolina was supported by the National Science Foundation through Grant GP-22887 and by the Materials Research Center of the University of North Carolina under Grant GH-33632 from the National Science Foundation.

Registry No. $[Co(salen)]_2$, 52951-34-5.

References and Notes

(1) R. DeIasi, S. L. Holt, and B. Post, *Inorg. Chem.*, **10**, 1498 (1971).
(2) S. Bruckner, M. Calligaris, G. Nardin, and L. Randaccio, *Acta Crystallogr., Sect. B*, **25**, 1671 (1961).
(3) M. Calvin and C. H. Barkelew, *J. Amer. Chem. Soc.*, **68**, 2267 (1946).
(4) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 338 (1959).
(5) S. Foner, *Rev. Sci. Instrum.*, **30**, 548 (1959).
(6) (a) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958); (b) H.-St. Rade, *J. Phys. Chem.*, **77**, 424 (1973).
(7) P. Selwood, "Magnetochemistry," 2nd ed, Interscience, New York, N. Y., 1956.
(8) J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press, London, 1932, Chapter IX.
(9) C. J. Ballhausen and A. D. Liehr, *J. Amer. Chem. Soc.*, **81**, 538 (1959).
(10) M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, **64**, 99 (1964).
(11) J. J. Alexander and H. B. Gray, *J. Amer. Chem. Soc.*, **89**, 3356 (1967).
(12) P. W. Anderson, *Phys. Rev.*, **115**, 2 (1959).

Killgore Research Center **Gene O. Carlisle***
West Texas State University **Gregory D. Simpson**
Canyon, Texas 79016

Department of Chemistry **William E. Hatfield***
University of North Carolina **Van H. Crawford**
Chapel Hill, North Carolina 27514 **Robert F. Drake**

Received July 10, 1974