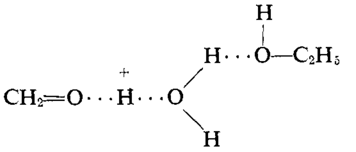
manner as to reduce the stabilizing influence of the methyl group. For these reactions the energy threshold for C–C bond cleavage is apparently below that for C–H bond cleavage.[13]

An intriguing feature of the induced fragmentations exemplified in reactions 1, 4, and 7 is that they provide a convenient and facile means of generating proton-bound dimers for further investigation, including particularly displacement reactions. Hence it is of interest to note that even though the basicity of formaldehyde (as measured by its proton affinity) is greater than that of either methyl fluoride or water, ethanol preferentially displaces methyl fluoride in reaction 2 and formaldehyde in reaction 5.[14] Intermediate I would provide a particularly favorable (and noncompetitive) pathway for the displacement of



$$\mathrm{CH_2{=}\overset{+}{O}\cdots H\cdots O(H)(H\cdots O(H){-}C_2H_5)}$$

I

formaldehyde from the proton-bound dimer of formaldehyde and water.

It is apparent from these observations that the strong hydrogen bond plays an important role in bimolecular reactions. Decomposition processes are rendered exothermic by virtue of the unusual stability gained in the product ions by the formation of a strong hydrogen bond. We are currently investigating the generality of these processes as well as the chemistry of the proton-bound dimers which they produce.

Acknowledgment. This work was supported in part by the United States Atomic Energy Commission under Grant No. AT(04-3)767-8.

---

(13) This argument does not imply that the methyl and hydrogen substituent effects are reversed. The proton affinity of CH_3CHO is 17 kcal/mol above that of CH_2O,[14] which may be attributed to stabilization of the carbonium ion center in CH_2OH^+ by methyl substitution. The threshold for CH_3CHOH^+ formation from $CH_3CH_2OH^+$ is only 7 kcal/mol below the threshold for CH_2OH^+ formation. Hence, it is necessary that the shift in charge density in the ionic product of reactions 2 and 4 reduce the methyl stabilization of the carbonium ion center to less than ~10 kcal/mol for C–C cleavage to become favored.

(14) The relevant proton affinities (kcal/mol) are: H_2O, 164;[15] CH_2O, 167;[11,15] CH_3CHO, 184;[11,15] and CH_3F, 151.[16]

(15) J. L. Beauchamp and S. E. Buttrill, Jr., *J. Chem. Phys.*, **48**, 1783 (1968).

(16) J. L. Beauchamp, D. Holtz, S. D. Woodgate, and S. L. Patt, *J. Amer. Chem. Soc.*, in press.

(17) D. P. Ridge is supported by the Department of Health, Education and Welfare, National Defense Education Act.

(18) Alfred P. Sloan Foundation Fellow, 1968–1970.

D. P. Ridge,[17] J. L. Beauchamp*[18]
Contribution No. 4282
Arthur Amos Noyes Laboratory of Chemical Physics
California Institute of Technology, Pasadena, California 91109

Received June 28, 1971

Parallel Spin Coupling *via* a Three-Atom Covalent Bridge in Di-μ-thiocyanato-tetrakis(ethylenediamine)dinickel(II) Iodide

Sir:

In all of the known cases of parallel (*i.e.*, ferromagnetic) spin coupling in cluster complexes, *e.g.*, $[Ni_3(acac)_6]$[1] and $[Ni_4(OCH_3)_4(acac)_4(CH_3OH)_4]$,[2] the exchange interaction takes place between two metal atoms linked by monatomic bridges and separated by ~3 Å. In the present communication we report the remarkable finding of ferromagnetic coupling, with an exchange integral $J = 5\ cm^{-1}$, between two Ni atoms in di-μ-thiocyanato-tetrakis(ethylenediamine)dinickel(II) iodide. The two Ni atoms are separated by 5.8 Å and are linked by two three-atom covalent bridges (NCS^-),[3] as illustrated schematically in Figure 1. Not only is this result unique for cluster complexes, but we believe that it is also novel for lattice ferromagnets. The closest analogy we are aware of for the latter class of compounds is the ferromagnetic interlayer interactions in $CrBr_3$,[4] and the intermolecular interactions in bis(*N*,*N*-diethyldithiocarbamato)iron(III) chloride.[5] The former act *via* two intervening Br^- ions over a distance of 7.05 Å, but the coupling parameters are only ~0.08 cm^{-1}, two orders of magnitude smaller than the effect we report here. The latter act between iron atoms about 7 Å apart over the path Fe—S···S—Fe with $J \sim 0.5°$.

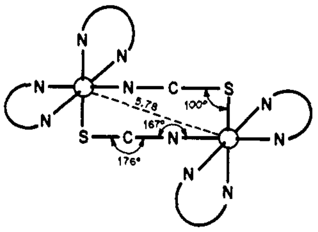


Figure 1. Schematic illustration of the structure of $[Ni_2(en)_4(SCN)_2]I_2$.

$[Ni_2(en)_4(SCN)_2]I_2$ was prepared[6] by crystallization from an aqueous ethanolic solution (50% v/v) containing equimolar amounts of $[Ni(en)_2(SCN)_2]$ and NaI. The product was twice crystallized from aqueous ethanol and found to analyze correctly. Magnetic susceptibility measurements were made between 1.5 and 300°K with a null-coil pendulum magnetometer[7] on three different samples contained in gelatin capsules. A magnetization curve determined at 1.65°K over the range 1–15.3 kOe showed the susceptibility to be field independent. A typical set of results is shown in Figure 2 in the form of plots of $\mu_{\text{eff}} = 2.8273(\chi_A'T)$ and $1/\chi_A'$. χ_A' is the susceptibility per gram atom of Ni and includes a diamagnetic correction[8] ($\chi_d = -157 \times 10^{-6}$ cm^3 g $atom^{-1}$). The estimated uncertainty in μ_{eff}, indicated by the error bars in the figure, is ±0.05 BM.

At 292°K, $\mu_{\text{eff}} = 3.04$ BM. As the temperature is decreased, μ_{eff} gradually increases until a maximum value of ~3.3 BM is reached at ~20°K. Below 7°K, μ_{eff} decreases rapidly, reaching 2.37 BM at 1.65°K. An $S' = 2$ state of a nickel dimer, in which all four e_g

---

(1) A. P. Ginsberg, R. L. Martin, and R. C. Sherwood, *Chem. Commun.*, 856 (1967); *Inorg. Chem.*, 7, 932 (1968).

(2) J. A. Bertrand, A. P. Ginsberg, R. I. Kaplan, C. E. Kirkwood, R. L. Martin, and R. C. Sherwood, *ibid.*, **10**, 240 (1971).

(3) A. E. Shvelashvili, M. A. Porai-Koshits, and A. S. Antsyshkina, *J. Struct. Chem.*, **10**, 552 (1969).

(4) E. J. Samuelsen, R. Silberglitt, G. Shirane, and J. P. Remeika, *Phys. Rev. B*, **3**, 157 (1971).

(5) H. H. Wickman, personal communication.

(6) A. V. Babaeva and C. Shou-Kang, *Zh. Neorg. Khim.*, **5**, 1274 (1960).

(7) R. M. Bozorth, H. J. Williams, and D. E. Walsh, *Phys. Rev.*, **103**, 572 (1956).

(8) P. W. Selwood, "Magnetochemistry," 2nd ed, Interscience, New York, N. Y., 1962, p 142.

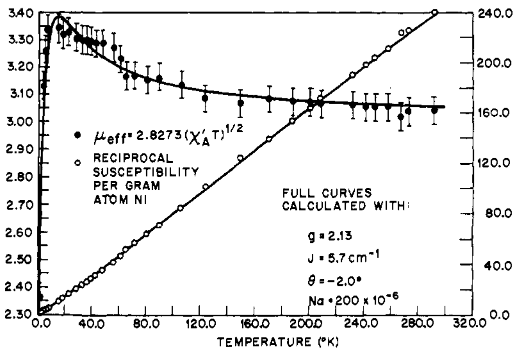


Figure 2. Temperature dependence of μ_{eff} (BM) per Ni atom and $1/\chi_A'$ for $[Ni_2(en)_4(SCN)_2]I_2$.

spins are coupled parallel, corresponds to a μ_{eff} of 3.46 BM per Ni atom for $g = 2$. Our results suggest that the dimer molecules are in a state of total spin $S' = 2$ below ~20°K, but the full value of μ_{eff} is not observed because of a lattice antiferromagnetic interaction which causes the observed decrease in moment at low temperatures. This conclusion is supported by comparison of the experimental results with the susceptibility equation for a nickel dimer

$$\chi_A' = \frac{3K}{T - \theta}\left[\frac{1 + 5e^{4J/kT}}{3 + 5e^{4J/kT} + e^{-2J/kT}}\right] + N\alpha$$

where J is the exchange integral, $N\alpha$ is the temperature-independent paramagnetism, $K = g^2N\beta^2/3k$, and θ is an effective Weiss constant included to take account of weak lattice interactions. The three sets of data were treated separately; the least-squares best fit to the susceptibility equation is obtained for $J = 7.4$–8.1° (≡5.1–5.6 cm^{-1}), $g = 2.08$–2.13, and $\theta = -2.2$ to $-2.0°$ with $N\alpha$ fixed at 200 × 10^{-6} cm^3 g-atom^{-1}. Figure 2 shows the comparison between experiment and theory; the agreement is satisfactory.

Further support for the conclusion that the two Ni atoms in $[Ni_2(en)_4(SCN)_2]I_2$ are ferromagnetically coupled to give an $S' = 2$ molecular ground state, and that the dimer molecules in this ground state engage in a lattice antiferromagnetic interaction, is provided by the magnetization curve ($\langle\mu\rangle$ dimer *vs.* H) determined at 1.65°K. The curve is linear and may be fitted to the molecular field theory equation

$$\langle\mu\rangle_{\mathrm{dimer}} = \frac{g^2\beta S'(S' + 1)H}{3k(T - \theta)}$$

for $g = 2.10$, $\theta = -2.7°$, and $S' = 2$, in agreement with the results described above.

In view of the long Ni–Ni distance in $[Ni_2(en)_4(SCN)_2]I_2$, it is clear that the exchange coupling must take place *via* the bridging thiocyanate groups. By analogy with the molecular orbital description of the isoelectronic molecule CO_2,[9] the ground state of NCS^- may be written as $(2s_N)^2(3s_S)^2(\sigma_s^b)^2(\sigma_z^b)^2(\pi_{x,y}^b)^4(\pi_{x,y})^4$, where the π orbitals are of the form $\pi_y^b = c_1 2p_{yN} + c_2 2p_{yC} + c_3 3p_{yS}$ and $\pi_y = c_4 2p_{yN} - c_5 3p_{yS}$, and the σ orbitals are $\sigma_s^b = c_6 2s_C + c_7 2p_{zN} + c_8 3p_{zS}$ and $\sigma_z^b = c_9 2p_{zN} + c_{10} 2p_{zC} + c_{11} 3p_{zS}$. From the point of view of Anderson's expanded-orbital theory,[10] assuming an idealized geometry with linear thiocyanate bridges and 90° N–Ni–S angles, the pathways for ferromagnetic coupling may be written $e_g(Ni_I)\|\sigma_z^b \perp \pi_y^b\|e_g(Ni_{II})$, $e_g(Ni_I)\|\sigma_z^b \perp \pi_y\|e_g(Ni_{II})$, $e_g(Ni_I)\|\sigma_s^b \perp \pi_y^b\|e_g(Ni_{II})$, and $e_g(Ni_I)\|\sigma_s^b \perp \pi_y\|e_g(Ni_{II})$, where $\|$ symbolizes overlap and $\perp$ represents orthogonality. The first of these pathways is exactly analogous to the principal pathway for ferromagnetic coupling in a monatomic 90° Ni–X–Ni bridge where a $2p_y$ atomic orbital is used instead of the three-center π_y^b orbital.[11] The other pathways are not present in a monatomic bridge, but occur here because the thiocyanate bridge is polynuclear.

It is particularly interesting to compare the exchange coupling in $[Ni_2(en)_4(SCN)_2]I_2$ with that in $[Ni_2(en)_4Cl_2]Cl_2$. The latter compound has a dimeric cation[12] with two Cl bridging atoms. The Ni–Cl–Ni angle was not reported in ref 12, but is not likely to deviate much from 90°. As expected, magnetic measurements show the molecular ground state to have $S' = 2$. From the susceptibility *vs.* temperature curve we find $J = 13°$ (≡9 cm^{-1}), $g = 2.15$, and $\theta = -2.2°$.

We conclude that the essential requirement for ferromagnetic coupling between Ni atoms is the availability of connecting orbitals of proper symmetry. If the connecting orbitals are multicenter molecular orbitals, the coupling can take place over long distances and through polyatomic bridges.

---

(9) R. S. Mulliken, *J. Chem. Phys.*, **3**, 720 (1935). For a simplified description see H. B. Gray, "Electrons and Chemical Bonding," W. A. Benjamin, New York, N. Y., 1964, pp 95–100.

(10) P. W. Anderson in "Magnetism," Vol. 1, G. T. Rado and H. Suhl, Ed., Academic Press, New York, N. Y., 1963, Chapter 2.

(11) See, for example, ref 1, where 90° Ni–O–Ni coupling is discussed.

(12) A. S. Antsyshkina and M. A. Porai-Koshits, *Dokl. Akad. Nauk SSSR*, **143**, 105 (1962).

A. P. Ginsberg,* R. C. Sherwood
Bell Telephone Laboratories, Incorporated
Murray Hill, New Jersey 07974

R. W. Brookes, R. L. Martin
Department of Inorganic Chemistry, University of Melbourne
Parkville 3052, Australia

Received July 13, 1971

Induced Circular Dichroism in Cholesteric Liquid Crystals

Sir:

During the past decade or so, there have been several reports of induced optical activity in inactive molecules either complexed to polypeptides while in a helical conformation[1-4] or noncomplexed in chiral solvents,[5,6] or as aggregated dyes.[7] This phenomenon has also been used for determining optical purities and absolute configurations.[8,9]

We wish to report that optically inactive molecules become chiral when dissolved in cholesteric liquid crystals, as detected by circular dichroism in

---

(1) E. R. Blout and L. Stryer, *Proc. Nat. Acad. Sci. U. S.*, **45**, 1591 (1959).

(2) L. Stryer and E. R. Blout, *J. Amer. Chem. Soc.*, **83**, 1411 (1961).

(3) E. R. Blout, *Biopolym. Symp.*, **No. 1**, 397 (1964).

(4) S. F. Mason and A. J. McCaffery, *Nature (London)*, **204**, 468 (1964).

(5) B. Bosnich, *J. Amer. Chem. Soc.*, **89**, 6143 (1967).

(6) L. D. Hayward and R. N. Totty, *Chem. Commun.*, 676 (1969).

(7) R. A. Berg and B. A. Haxby, *Mol. Cryst. Liquid Cryst.*, **12**, 93 (1970).

(8) W. H. Pirkle, *J. Amer. Chem. Soc.*, **88**, 1837 (1966).

(9) W. H. Pirkle and S. D. Beare, *ibid.*, **90**, 6250 (1968).