

stability (decreased reactivity) of the cyclopropylcarbinyl cation.

In line with the strong supporting evidence for the intermediacy of a metal-bonded carbonium ion⁶-metal-complexed carbene hybrid intermediate^{5,11} in the transition metal promoted rearrangement of derivatives of bicyclo[1.1.0]butane in nonprotic solvents, it is tempting to view the formation of **6b** and **6c** as resulting from solvent capture by a carbenoid type resonance hybrid. Such a hybrid would result from a **1b** → **7** → **8** type transformation as shown above. In order to test this concept, we studied the isomerization of **1b** in methanol-*O-d*. If **8** were the precursor of **6b**, the use of methanol-*O-d* would result in the methoxy group and the deuterium residing exclusively at the homoallylic position. In methanol-*O-d*, the addition of either rhodium dicarbonyl chloride dimer or silver fluoroborate resulted in the conversion of **1b** into **9** and an approximately equimolar mixture of **10** and **11**. The formation of both **10** and **11** required either that protonolysis of the intermediate, **7**, occur prior to the formation of homoallylic product or that **1b** be directly converted to **12** in an acid-catalyzed reaction. Either process would result in the formation of **12**, which can subsequently cleave *via* path a and path b to yield **10** and **11**,¹² respectively. These results indicated that, at least in the case of **1b**, no metal-bonded carbonium ion-metal-complexed carbene resonance hybrid is formed in protic solvent, in stark contrast to the formation of such a resonance hybrid in nonprotic solvents. Thus, protic solvents can completely change the mechanism of transition metal complex promoted rearrangements of highly strained ring systems.

We have also found that **1c** reacts readily on addition of small amounts of either rhodium dicarbonyl chloride dimer or silver fluoroborate in methanol-*O-d* to yield **13** as the only product. Current experimental results do not allow us to determine whether **13** is derived *via* the **1c** → **14** → **15** route, *via* the **1c** → **14** → **16** path, or directly through a **1c** → **15** process involving protonation. The question which remains to be answered in this case is whether the added transition metal derivatives are the active reagents or whether these complexes are reacting with solvent to generate protic acid or some other new reagent which promotes the observed reactions. We are continuing to investigate this problem.¹³

Acknowledgment. We are indebted to the National Science Foundation for partial support of this investigation.

(11) P. G. Gassman, T. J. Atkins, and F. J. Williams, *J. Amer. Chem. Soc.*, **93**, 1812 (1971).

(12) The ratio of **10**:**11** was determined by nmr spectroscopy. The approximately equal amounts of **10** and **11** are consistent with secondary α and β deuterium isotope effects being small and approximately the same in carbonium ion reactions: E. A. Halevi, *Progr. Phys. Org. Chem.*, **1**, 127 (1963).

(13) NOTE ADDED IN PROOF. Subsequent to the acceptance of this communication, it has been suggested that intermediates such as **7** and **14** would not be formed with rhodium complexes, but might be formed with silver(I) in methanol [W. G. Dauben and A. J. Kielbania, Jr., *J. Amer. Chem. Soc.*, **94**, 3669 (1972)]. If this suggestion can be substantiated, two different mechanisms would be implicated for the conversion of **1b** into a mixture of **9**, **10**, and **11** [one for the rhodium(I) complex and one for silver(I)].

(14) The Ohio State University Postdoctoral Fellow, 1970-1971.

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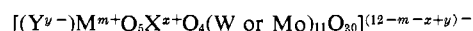
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Isomorphous Heteropoly Complexes Containing Various Pairs of Paramagnetic Atoms. Exchange-Coupled Differing Spins with Absence of Long-Range Magnetic Interactions. A New Class of Paramagnetic Behavior. Theoretical Treatment. Novel Geometrical Isomerism

Sir:

In 1966 a large new structural category of heteropoly complexes was fully established:^{1,2} the biheteroatom 11-heteropoly anions



of structure^{1,3} shown in Figure 1. That paper¹ also reported then-unexplained unique paramagnetic behavior, for $K_7[(H_2O)Co^{2+}O_5Co^{3+}O_4W_{11}O_{30}] \cdot 12H_2O$, for which the susceptibility changed only 13% between -143 and 23° .

Subsequently, others⁴⁻⁹ reported many derivatives (various M's and X's) formulated according to this proven^{1,2} structure. Only one of those new compounds contained two paramagnetic atoms: $[(H_2O)Ni^{2+}O_5Fe^{3+}O_4W_{11}O_{30}]^{7-}$, similar unexplained antiferromagnetic behavior being noted.⁷ In 1970 the original structural interpretation was extended.³

The present paper shows that the biheteroatom 11-heteropoly complexes offer a clearly propitious area for study of paramagnetic interactions. *Via* suitable substitutional routes, salts of pure complexes may be made containing a very wide variety of pairs of paramagnetic heteroatoms. Subtle variations may be made by using various Y's or by substituting Mo's for W's. All the complexes are isomorphous, obviating a major obstacle to comparative interaction studies. Long-range magnetic order effects are neither expected nor found. Thus many paramagnetic interactions may be clearly and systematically studied, e.g., for relative J 's, in exactly comparable circumstances.

Isomorphous compounds prepared,^{10,11} fully analyzed,^{10,11} and studied in the present work, some containing complexes which are geometrical isomers of a new and significant sort, were:¹² I, $K_7[(H_2O)Fe^{3+}O_5Co^{2+}O_4W_{11}O_{30}] \cdot 14H_2O$; II, $K_7[(H_2O)Co^{2+}O_5Fe^{3+}O_4W_{11}O_{30}] \cdot 13H_2O$; III, $K_6[(H_2O)Fe^{3+}O_5Co^{3+}O_4W_{11}O_{30}] \cdot 13H_2O$; IV, $K_7[(H_2O)Co^{2+}O_5Co^{3+}O_4W_{11}O_{30}] \cdot 12H_2O$; V, $(NH_4)_8[(H_2O)Co^{2+}O_5Co^{2+}O_4W_{11}O_{30}] \cdot 13H_2O$; VI, $K_6[(H_2O)Co^{3+}O_5Fe^{3+}O_4W_{11}O_{30}] \cdot 18H_2O$. Ligand field spectra^{10,11} confirm the coordination geometries,

(1) L. C. W. Baker, *et al.*, *J. Amer. Chem. Soc.*, **88**, 2329 (1966).

(2) L. C. W. Baker, *Proc. Int. Conf. Coord. Chem.*, **9th**, 1966, 421 (1966).

(3) L. C. W. Baker and J. S. Figgis, *J. Amer. Chem. Soc.*, **92**, 3794 (1970).

(4) T. J. R. Weakley and S. A. Malik, *J. Inorg. Nucl. Chem.*, **29**, 2935 (1967).

(5) S. A. Malik and T. J. R. Weakley, *Chem. Commun.*, 1094 (1967); *J. Chem. Soc. A*, 2647 (1968).

(6) R. Ripan and M. Puscasu, *Z. Anorg. Allg. Chem.*, **358**, 83 (1968).

(7) M. Puscasu, D.Sc. Dissertation, Academy of the Socialist Republic of Romania, Institute of Chemistry, Cluj Section, Romania, 1969.

(8) C. Tourné, *C. R. Acad. Sci., Ser. C*, **266**, 702 (1968).

(9) C. Tourné and G. Tourné, *ibid.*, **266**, 1363 (1968); *Bull. Soc. Chim. Fr.*, 1124 (1969).

(10) V. E. Simmons, Doctoral Dissertation, Boston University, 1963.

(11) S. H. Wasfi, Doctoral Dissertation, Georgetown University, 1971.

(12) In these compounds small differences in the numbers of the zeolytic waters of hydration do not affect the isomorphism, nor do small differences in numbers of simple cations, some of which are in the zeolytic channels.

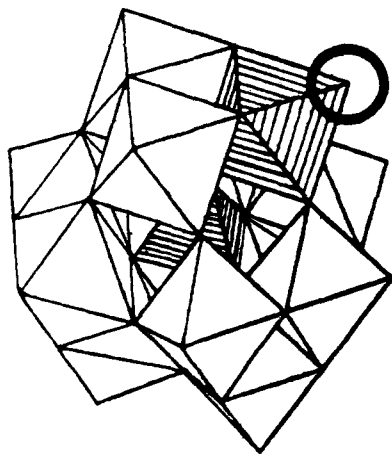


Figure 1. The structure of the biheteroatom 11-heteropoly complexes,^{1,3} $[(Y^{v-})M^{m+}O_5X^z+O_4(W \text{ or } Mo)_{11}O_{30}]^{(12-m-z+v)-}$. The hatched (upper right) octahedron contains the heteroatom M^{m+} . Each of the other 11 octahedra contains W or Mo. The heteroatom X^{z+} is within the central hatched tetrahedron, bridged to M^{m+} by an O. The circled vertex locates the center of that atom of a ligand, Y^{v-} , which is coordinated to M^{m+} . All of the other vertices locate the centers of close-packed O atoms (39 in number). In all of the complexes studied in the present work, Y was H_2O . The representation shows regular polyhedra. In the actual complexes, the W or Mo octahedra, which share corners and edges, are all considerably distorted by movement of the metal atoms far off center in the octahedra, toward the unshared vertices.²⁵⁻²⁷ The distorted W or Mo octahedra severely distort the M^{m+} octahedron, removing its center of symmetry, as revealed by spectra.¹⁰ The X^{z+} to M^{m+} distance is about 3.3 Å and the X^{z+} -O- M^{m+} angle is about 125°.

as do acidifications, which quantitatively expel M^{m+} ions and yield the respective $[X^{z+}O_4W_{12}O_{36}]^{(8-z)-}$ anions.

Theory (below) and antiferromagnetic data show that low T susceptibilities when $S_1 \neq S_2$ follow a Curie law characteristic of $|S_1 - S_2|$ and the individual g 's; high T susceptibilities asymptotically approach another Curie law, characteristic of the sum of the susceptibilities of the uncoupled atoms; while in broad intermediate T ranges the susceptibility changes remarkably little. We know of no comparable examples.

Others¹³⁻¹⁹ have given theoretical treatments for various isolated groupings of coupled paramagnetic atoms, but these apply only when the g 's, and usually also the S 's, are equal. Also, experimental confirmations for pure compounds have usually not involved the stringent test of fitting susceptibilities both above and far below liquid N_2 temperature.

A theoretical treatment for the more general case, yielding a closed form for the susceptibility when S_1 , S_2 , g_1 , g_2 , and J (isotropic) have independent values in isolated coupled pairs of atoms 1 and 2, may be obtained, using the simplest form of exchange coupling, by assuming the Hamiltonian $\mathcal{H} = \beta(g_1S_1 + g_2S_2) \cdot H - JS_1 \cdot S_2$. The magnetic susceptibility of the system

(13) B. Bleaney and K. D. Bowers, *Proc. Roy. Soc., Ser. A*, 214, 451 (1952).

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(15) A. Earnshaw and J. Lewis, *J. Chem. Soc.*, 396 (1961).

(16) K. Kambe, *J. Phys. Soc. Jap.*, 5, 48 (1950).

(17) J. Yvon, J. Horowitz, and A. Ahragim, *Rev. Mod. Phys.*, 25, 165 (1953).

(18) T. Tsang, *et al.*, *J. Phys. Chem. Solids*, 32, 1441 (1971).

(19) B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, 6, 37 (1964).

defined by this Hamiltonian seems not to have been reported previously.

A derivation,²⁰ similar to one used^{21,22} for calculating orbital and spin contributions to susceptibility of an atom, yields

$$\chi = \frac{\sum_S (2S + 1) \chi_S e^{JS(S+1)/2kT}}{\sum_S (2S + 1) e^{JS(S+1)/2kT}}$$

wherein the sum on S extends in unit steps from $|S_1 - S_2|$ to $S_1 + S_2$ and χ_S is

$$\chi_S = \frac{N\beta^2}{3kT} \left\{ S(S+1)[g_1\gamma + g_2(1-\gamma)]^2 + \frac{kT}{J}(g_1 - g_2)^2 \gamma(\gamma - 1) \right\} \text{ for } S \neq 0$$

$$\chi_0 = \frac{2N\beta^2}{3J}(g_1 - g_2)^2 S_1(S_1 + 1) \text{ for } S = 0$$

$$\gamma = [S(S+1) + S_1(S_1+1) - S_2(S_2+1)]/2S(S+1)$$

More familiar results occur if $g_1 = g_2$. When $g_1 \neq g_2$ the Zeeman and exchange terms of \mathcal{H} do not commute and a T -independent part appears in each χ_S , arising from Zeeman interaction connecting exchange terms differing in S by ± 1 .

For the low-temperature limit when $S_1 \neq S_2$ and the ground state has spin S_0 , the Curie susceptibility is

$$\chi = \frac{N\beta^2 S_0(S_0 + 1) g_{\text{eff}}^2}{3kT} \text{ when } kT \ll J$$

where $g_{\text{eff}} =$

$$\frac{1}{2}(g_1 + g_2) + \frac{1}{2}(g_1 - g_2) \frac{S_1(S_1 + 1) - S_2(S_2 + 1)}{S_0(S_0 + 1)}$$

The high-temperature asymptotic limit is given by

$$\chi = \frac{N\beta^2}{3kT} [g_1^2 S_1(S_1 + 1) + g_2^2 S_2(S_2 + 1)]$$

The wide span of the energy states, $\approx J(S_1 + S_2)^2/2$, leads to gradual transition between the low- and high-temperature Curie law limits and hence to a broad temperature range wherein susceptibility changes little.

Single-crystal X-ray structure²³ and powder data^{10,11} show I-VI isomorphous, having the structure reported earlier:¹ F-centered cubic, $Z = 8$, with X-M axes disordered over their 12 possible orientations. The closest approach of centers of O atoms from adjacent complexes is over 3.5 Å. That is decidedly greater than the usual van der Waals oxygen separation and undoubtedly results from heavy polarization of the exterior O atoms toward the W^{6+} atoms, producing negligible van der Waals attractions between complexes, which are, in effect, relatively isolated chemically bonded systems with very small possibilities for long-range magnetic interactions.

Slopes and shapes of the theoretical curves are very sensitive to the values of S and of g . Good agreements between theoretical curves and experimental suscepti-

(20) The full derivation is quoted in ref 11.

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(22) R. M. Golding, "Applied Wave Mechanics," Van Nostrand, New York, N. Y., 1969, Chapter 6.

(23) L. L. Koh, Doctoral Dissertation, Boston University, 1963.

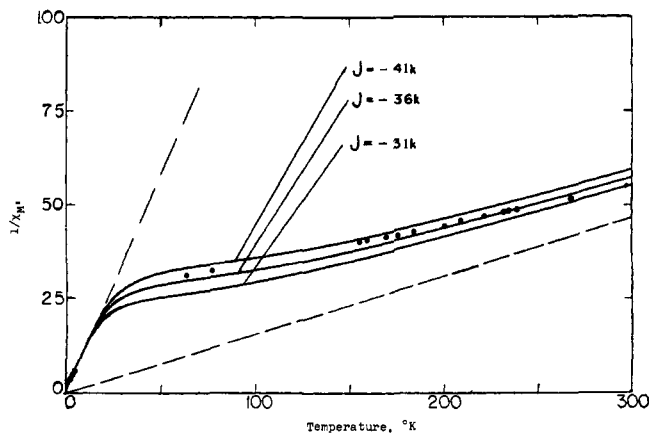


Figure 2. For $K_7[(H_2O)Fe^{3+}O_5Co^{2+}O_4W_{11}O_{36}] \cdot 14H_2O$. Points represent experimental susceptibilities, corrected for Co's TIP and for diamagnetism on basis of adjustment of experimental diamagnetism¹⁰ of $K_4[SiO_4W_{12}O_{36}] \cdot 11H_2O$. Solid lines are susceptibility behaviors predicted by the theory, using S and g values in the last paragraph of the text, for three values of J/k (in $^\circ K$). Dashed lines are the theoretical asymptotically approached limiting Curie laws for low and for high T 's.

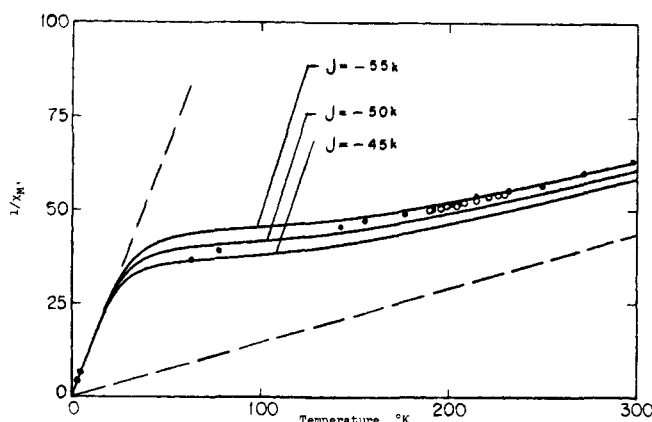


Figure 3. For $K_7[(H_2O)Co^{2+}O_5Fe^{3+}O_4W_{11}O_{36}] \cdot 13H_2O$. Points represent corrected (for Co's TIP and for diamagnetism) experimental susceptibilities. Filled dots taken in order of decreasing T , open dots in order of increasing T . Solid lines are susceptibility behaviors predicted by the theory, using S and g values in the last paragraph of the text, for three values of J/k (in $^\circ K$). Dashed lines are the theoretical asymptotically approached limiting Curie laws for low and for high T 's.

bilities from 2 to 300 $^\circ K$ were obtained for I-V using a single set of S 's and g 's obtained independently from spectra and/or magnetic behaviors of isomorphous complexes containing only one paramagnetic atom apiece.^{10,11}

For $Fe^{3+}(\text{oct or tet})$, $S = 5/2$, $g = 2.0$. For $Co^{2+}(\text{tet})$, $S = 3/2$, $g = 2.2$. For $Co^{2+}(\text{oct})$, $S = 3/2$, $g = 2.4$. For $Co^{3+}(\text{tet})$, $S = 2$, $g = 2.07$.²⁴ Figures 2-4, for I,

(24) The X-ray structure^{25,26} of hexagonal $K_5[Co^{3+}O_4W_{12}O_{36}] \cdot 20H_2O$ shows the $Co^{3+}O_4$ tetrahedron has Jahn-Teller elongation, whereas the $Si^{4+}O_4$ in isomorphous¹² $K_4[Si^{4+}O_4W_{12}O_{36}] \cdot 18H_2O$ is regular.²⁷ Thus the $Co^{3+}O_4$ elongation is not caused by crystal packing forces. These complexes are isomorphous with the biheteroatom 11-heteropoly species ($M^{m+} = W^{6+}$ and $Y^{n-} = O^{2-}$). $K_5[Co^{3+}O_4W_{12}O_{36}] \cdot 20H_2O$ follows very precisely a Curie-Weiss law ($\theta = -1.1 \pm 0.5$) with $g = 2.07$. The increase of g above 2.00 and the negative θ coincide with elongation of the $Co^{3+}O_4$ in accordance with theory.¹⁰ Isomorphous $K_5H[Co^{2+}O_4W_{12}O_{36}] \cdot 15H_2O$, containing a regular $Co^{2+}O_4$ tetrahedron,²⁸ precisely follows a Curie law with $g = 2.20$.

(25) N. F. Yannoni, Doctoral Dissertation, Boston University, 1961.

(26) L. C. W. Baker in "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., Macmillan, New York, N. Y., 1961, p 608.

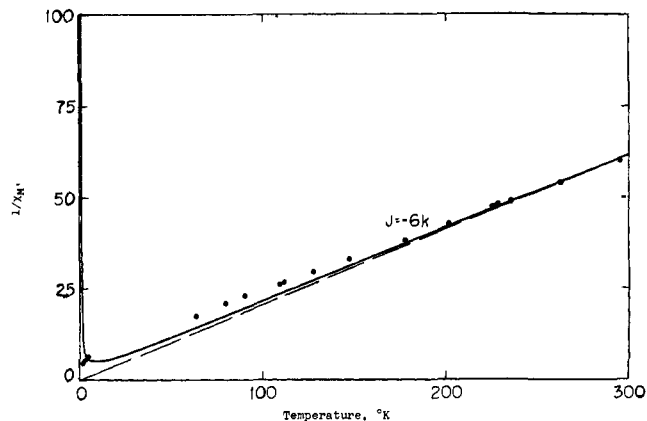


Figure 4. The shape when $S_1 = S_2$. For $(NH_4)_3[(H_2O)Co^{2+}O_5Co^{2+}O_4W_{11}O_{36}] \cdot 13H_2O$. Points represent experimental susceptibilities, corrected for Co's TIP's and for diamagnetism. Solid line is behavior predicted by the theory for $S_1 = S_2 = 3/2$ and unequal g values in the last paragraph of the text. Dashed line is predicted limiting Curie law for rising T . Theory predicts that $1/\chi_M$ should go through a minimum at very low T . The predicted rise in $1/\chi_M$ with decreasing T at very low T was not observed down to 2 $^\circ K$. A small amount of paramagnetic impurity could account for that.

II, and V, show typical results. For III, $J/k = -36 \pm 5^\circ K$. For IV (partial data published¹), $J/k = -72 \pm 5^\circ K$. $K_5[Fe^{3+}O_4W_{12}O_{36}] \cdot 15H_2O$ and VI each follow simple Curie law to 2 $^\circ K$ for spin-only $S = 5/2$, since $Co^{3+}(\text{oct})$ is diamagnetic.

(27) P. Smith, Doctoral Dissertation, Georgetown University, 1971.

(28) L. C. W. Baker and V. E. Simmons, *J. Amer. Chem. Soc.*, **81**, 4744 (1959).

(29) Addressee for reprints and correspondence, at Georgetown University.

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Interpretation of Photoelectron Spectra of Hydrocarbons by Use of a Semiempirical Calculation

Sir:

The interpretation of photoelectron spectra of organic molecules has appeared to be more difficult than expected as the present nonempirical and semiempirical theories give orbital energies that usually differ very much from the observed ionization potentials. In the comparison of experiment and theory it has therefore appeared to be necessary to introduce empirical corrections of different kinds.

To avoid this we have tried to parametrize the semiempirical procedure, INDO, to get agreement with photoelectron-spectroscopic ionization potentials.

The new procedure, SPINDO (spectroscopic potentials adjusted INDO),¹ can briefly be described as MINDO^{2,3} with the following changes for a hydro-

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(2) N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, **50**, 1262 (1969).

(3) N. C. Baird, Program 137, Quantum Chemistry Program Exchange, Indiana University, 1968.