Cu(2,7-dimethyl-1,8-naphthyridine)$_2$ClO$_4$ (A).—A solution of 0.14 g of cupric perchlorate hexahydrate in 40 ml of absolute methanol and 10 ml of 2,2'-dimethoxypropane was refluxed for 6 hr, and 0.158 g of dmNN was added. The solution was then refluxed for 18 hr more, and the resultant brown solution was permitted to cool slowly. The brown needles were collected by filtration, washed with chloroform, and dried over calcium chloride. The compound could be recrystallized from methanol or nitromethane. This preparation is essentially that given in ref 1 for Cu(dmNN)$_3$(ClO$_4$)$_2$. *Anal.* Calcd for Cu(C$_{10}$H$_{10}$N$_2$)$_2$ClO$_4$: Cu, 13.25; C, 50.11; H, 4.21; ClO$_4^-$, 20.75. Found: Cu, 12.98; C, 50.20; H, 4.25; ClO$_4^-$, 20.69.

Cu$_2$(NN)Cl$_2$ and Cu$_2$(dmNN)Cl$_2$.—To a solution of 0.198 g of CuCl in 40 ml of warm acetonitrile 0.065 g of NN or 0.079 g of dmNN in 10 ml of acetonitrile was added. The product precipitated immediately and was filtered, washed with absolute methanol, and air-dried. No suitable solvent was found for recrystallization. Air oxidation during the preparation occurred with these compounds, but pure products could be obtained easily by carrying out the synthesis under dry nitrogen. *Anal.* Calcd for Cu$_2$(C$_8$H$_6$N$_2$)Cl$_2$: Cu, 38.73; C, 29.28; H, 1.85. Found: Cu, 38.83; C, 29.36; H, 1.62. Calcd for Cu$_2$(C$_{10}$H$_{10}$N$_2$)Cl$_2$: Cu, 35.68; C, 33.72; H, 2.83. Found: Cu, 35.39; C, 34.45; H, 2.85.

Analyses.—Carbon and hydrogen analyses were performed by Chemalytics, Inc., Tempe, Ariz. Copper was determined volumetrically either by iodometry or with EDTA after oxidation to the 2+ state. ClO$_4^-$ was determined by passing the sample through a cation exchanger in H$^+$ ion form and titrating the resultant acid solution with standard NaOH.

Magnetic Measurements.—Magnetic susceptibilities were determined by the Gouy method using an apparatus which has been described elsewhere.[3]

Spectra.—Infrared spectra were taken of pressed KBr disks using a Beckman IR-20 infrared spectrometer. Visible and uv spectra were taken on a Cary 14 recording spectrophotometer.

(3) C. C. Houk and K. Emerson, *J. Inorg. Nucl. Chem.*, **30**, 1493 (1968).

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Magnetic Exchange in Transition Metal Complexes. VIII.[1] Molecular Field Theory of Intercluster Interactions in Transition Metal Cluster Complexes

Sir:

The principal reason for the current interest in the magnetic properties of transition metal cluster complexes[2] is the fact that exchange coupling between unpaired spins on the metal atoms is predominantly an intracluster effect. In the case of orbital-singlet ground-state clusters this makes possible an exact solution of the cluster susceptibility problem and the derivation of reliable exchange integrals from experimental susceptibility *vs.* temperature data. However, recent experimental results[3-6] have made it clear that under certain conditions intercluster interactions can have a significant effect at temperatures below about 50°K. Important intercluster effects occur in complexes with weak ferromagnetic intracluster exchange. These clusters, in their spin aligned states, couple collectively and thus change the form of the cluster susceptibility curve in the low-temperature region. Since the low-temperature part of the curve may be important in obtaining a reliable value for the intracluster exchange integral, it is necessary to take account of the intercluster exchange in the theoretical susceptibility equation.

The effect of intercluster exchange has been included in the cluster susceptibility equation by introducing an empirical Weiss constant.[3-6] Thus, if the susceptibility per gram atom, χ_A', of an n-atom cluster is written in the general form

$$\chi_A' = \frac{Ng^2\beta^2}{nkT}F(J,T) \qquad (1)$$

where $F(J,T)$, defined in the next section, is a function of the exchange integrals and the temperature, intercluster exchange is represented by replacing T with $T - \theta$ in the factor $Ng^2\beta^2/nkT$. In the present note we derive the correction for intercluster exchange in the molecular field approximation. The correction is temperature dependent, but it is found that for weak intercluster interactions, such as have so far been observed, the procedure of replacing T by $T - \theta$ is adequate.

In the absence of intercluster coupling, the isotropic exchange Hamiltonian for an n-atom cluster in an external magnetic field H along the z direction may be written

$$\mathcal{H} = \left(\sum_{i=1}^{n}\sum_{j>i}^{n} -2J_{ij}\hat{s}_i\cdot\hat{s}_j\right) - g\beta H\hat{S}^z \qquad (2)$$

J_{ij} is the exchange integral for the interaction between the metal atoms with spin operators $\hat{s}_i$ and $\hat{s}_j$; $\hat{S}^z$ is the operator for the z component of total cluster spin. To include intercluster exchange we add to (2) the term $-2z'J'\hat{S}_i\cdot\hat{S}_j$, where J' is the effective intercluster exchange integral and z' is the cluster lattice coordination number. The molecular field approximation allows us to write

$$\hat{S}_i\cdot\hat{S}_j = \hat{S}_i^z\langle\hat{S}_j^z\rangle \qquad (3)$$

The Hamiltonian including intercluster exchange in the molecular-field approximation is therefore

$$\mathcal{H} = \left(\sum_{i=1}^{n}\sum_{j>i}^{n} -2J_{ij}\hat{s}_i\cdot\hat{s}_j\right) - g\beta H\hat{S}^z - 2z'J'\hat{S}^z\langle\hat{S}^z\rangle \qquad (4)$$

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(1) Part VII: M. E. Lines, A. P. Ginsberg, R. L. Martin, and R. C. Sherwood, *J. Chem. Phys.*, **57**, 1 (1972).

(2) For reviews see (a) A. P. Ginsberg, *Inorg. Chim. Acta Rev.*, **5**, 45 (1971); (b) R. L. Martin in "New Pathways in Inorganic Chemistry," E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Ed., Cambridge University Press, London, 1968, Chapter 9.

(3) A. P. Ginsberg, R. L. Martin, and R. C. Sherwood, *Inorg. Chem.* **7**, 932 (1968).

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

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Symbolize the eigenvalues of (2) in zero field by $E_0(S,M_S)$, where M_S are the eigenvalues of $\hat{S}^z$. The eigenvalues of (4) may now be written

$$E(S,M_S) = E_0(S,M_S) - g\beta HM_S - 2z'J'M_S\langle\hat{S}^z\rangle \quad (5)$$

The expectation value of the z component of total cluster spin is defined by

$$\langle\hat{S}^z\rangle = \sum_S \sum_{M_S} M_S e^{-E(S,M_S)/kT}/\mathrm{PF} \quad (6)$$

where PF is the partition function

$$\mathrm{PF} = \sum_S \sum_{M_S} e^{-E_0(S,M_S)/kT} \quad (7)$$

and the index S runs over all allowed values of total spin including any remaining degeneracy. By expanding the exponentials $e^{g\beta HM_S/kT}$ and $e^{2z'J'M_S\langle\hat{S}^z\rangle/kT}$, neglecting terms beyond the second, we obtain from (6) an implicit equation in $\langle\hat{S}^z\rangle$ which is easily solved to give

$$\langle\hat{S}^z\rangle = g\beta H\mathrm{F}(J,T)/[kT - 2z'J'\mathrm{F}(J,T)] \quad (8)$$

where

$$\mathrm{F}(J,T) = \sum_S \sum_{M_S} M_S^2 e^{-E_0(S,M_S)/kT}/\mathrm{PF} \quad (9)$$

The susceptibility equation follows as

$$\chi_A' = Ng^2\beta^2\mathrm{F}(J,T)/n[kT - 2z'J'\mathrm{F}(J,T)] \quad (10)$$

Comparison of eq 10 with the $T - \theta$ form of eq 1 shows that

$$\theta = 2z'J'k^{-1}\mathrm{F}(J,T) \quad (11)$$

The correction θ therefore has a temperature dependence determined by $\mathrm{F}(J,T)$ for the cluster. Numerical calculations with $\mathrm{F}(J,T)$ for several different clusters show that so long as $z'J' \ll J$, the approximation of taking θ to be a constant is satisfactory. To illustrate this we compare in Table I the least-squares best-fit parameters for the susceptibility *vs.* temperature (1.5–298°K) data of $[Ni_2(en)_4(SCN)_2]I_2$ and $[Ni_2(en)_4Cl_2]Cl_2$, obtained (A) on the assumption of constant θ[6] and (B) from eq 10.[7]

TABLE I

COMPARISON OF LEAST-SQUARES BEST-FIT PARAMETERS FOR SUSCEPTIBILITY *vs.* TEMPERATURE DATA[a]

	A			B		
Compound[6,7]	g	J, °K	θ, °K	g	J, °K	$Z'J'$, °K
$[Ni_2(en)_4(SCN)_2]I_2$	2.14[b]	7.6[b]	−2.0	2.14	7.2	−0.51
$[Ni_2(en)_4Cl_2]Cl_2$	2.15	13.3	−2.2	2.14	13.8	−0.54

[a] (A) Assuming constant θ and (B) from eq 10. [b] The value in ref 6 is slightly different because an error in the diamagnetic susceptibility correction gave χ_A' values uniformly low by 50×10^{-6} cm^3 g-atom^{-1}; this has been corrected in ref 7.

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(7) A. P. Ginsberg, R. L. Martin, R. W. Brookes, and R. C. Sherwood, *Inorg. Chem.*, in press.

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Pressure Effects on the Ligand-Field Spectra of Nickel(II) and Cobalt(II) Five-Coordinate Complexes of the Type ML_3X_2[1]

Sir:

Recently,[2] the effects of high external pressures on the ligand-field spectra of some five-coordinate Ni(II) complexes involving tetradentate, tridentate, and bidentate ligands were investigated. It was found that the spectra of the complexes with trigonal-bipyramidal (TBP) structures were much more sensitive to pressure than those having the square-pyramidal (SqPy) structures. For C_{3v} symmetry the low-energy band (ν_1), corresponding to the transition $^1A_1 \rightarrow a'E$, shifted toward higher energy, and in many cases the band became more symmetrical with increasing pressure. The technique was suggested as a means of distinguishing between TBP and SqPy structures.

Pressure effects of related five-coordinate complexes involving monodenate ligands have not been studied. This paper reports on such a study made with six Ni(II) and two Co(II) complexes. Table I summarizes the pressure dependences of several ML_3X_2 complexes, where M = Ni(II), Co(II); L = Me_3P, Ph_2PH, Ph_2PCH_3; and X = Cl, Br, I, CN. The results are compared with structural determinations made by X-ray measurements. For all pressure dependences which range from 8 to 29 cm^{-1}/kbar a distorted TBP–SqPy structure has been determined. The complex $Ni(Me_3P)_2I_2$ is observed to show a high pressure dependence of 35 cm^{-1}/kbar. The structure of this complex is unknown. Based on previous measurements,[2] we would suggest a TBP structure for the complex. Unpublished ambient pressure infrared data[3] appear to confirm this. This would preclude the possibility of conversion to a TBP structure occurring with pressure for this complex. Table II tabulates the dν/dp values for several five-coordinate nickel(II) complexes involving ligands varying from a tetradentate to a monodentate type. It may be observed that a general trend exists and that the highest pressure dependences are observed for a complex involving a TBP structure with

TABLE I

PRESSURE DEPENDENCE OF ML_3X_2 COMPOUNDS

Complex	Structure by X-ray data	dν/dp, cm^{-1}/kbar
$Ni(Me_3P)_3Br_2$	Distorted,[a] TBP–SqPy[b]	19
$Ni(Me_3P)_3I_2$	Undetermined[c]	35
$Ni(Ph_2PH)_3Cl_2$	Distorted, TBP–SqPy[d]	29
$Ni(Ph_2PH)_3Br_2$	Distorted, TBP–SqPy[d]	27,[e] 29[f]
$Ni(Ph_2PH)_3I_2$	Distorted, TBP–SqPy[d]	17,[e] 27[f]
$Ni(Ph_2PMe)_3(CN)_2$	Distorted, TBP–SqPy[g]	20
$Co(Ph_2PH)_3Br_2$	Distorted, TBP–SqPy[d]	8
$Co(Ph_2PH)_3I_2$	Distorted, TBP–SqPy[d]	23

[a] Determined from visible absorption studies. [b] B. B. Chastain, D. W. Meek, E. Billig, J. E. Hix, and H. B. Gray, *Inorg. Chem.*, **7**, 2412 (1968). [c] Unpublished infrared data supports TBP structure.[3] [d] J. A. Bertrand and D. L. Plymale, *Inorg. Chem.*, **5**, 879 (1966). [e] High-frequency peak. [f] Low-frequency peak. [g] J. K. Stalick and J. A. Ibers, *Inorg. Chem.*, **8**, 1084 (1969).

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(1) Based on work performed under auspices of U. S. Atomic Energy Commission.

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