$Co(Et_2(dtc))_3$ undergoes a one-electron oxidation at +0.949 V in addition to a similar but irreversible reduction at −1.07 V in DMF. Lastly, it is noted that the complexes $M(R_1R_2(dtc))_2(S_2C_2R_2)^z$[35] (M = Fe, Ru; R = CF_3, CN) exist as a four-membered electron-transfer series (z = 2−, 1−, 0, 1+). The stabilization of M(IV) in either of the two highest oxidation levels is currently under investigation.[36]

Acknowledgments.—This research was supported by the National Science Foundation under Grant GP-18978X. We thank Professor H. Taube for a copy of ref 20a prior to its publication.

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Correspondence

Copper(I) Complexes of 1,8-Naphthyridine

Sir:

Recently it was reported[1] in this journal that cupric perchlorate forms a tris complex with 2,7-dimethyl-1,8-naphthyridine (dmNN) having the formula $Cu(dmNN)_3(ClO_4)_2$ (A). Analytical data, a uv spectrum and a partial list of infrared spectral bands were given in the paper. No magnetic data were reported. The color of the compound was described as brown.

An attempt was made in this laboratory to duplicate this synthesis using the parent 1,8-naphthyridine (NN) instead of dmNN. The initial attempts failed, but by varying the described conditions of the reaction, an orange compound B was obtained. This compound proved on elemental analysis to be a copper(I) perchlorate complex of NN. It was diamagnetic, and spectra of solutions in acetonitrile and nitromethane showed no bands in the region 8000–15,000 cm^{-1} in which copper(II) usually absorbs.

As a result of this experience, a sample of 2,7-dimethyl-1,8-naphthyridine was prepared and the synthesis reported in ref 1 was duplicated exactly. The reaction proceeds just as described and yields a brown product (A′), but elemental analysis indicated this compound is also a complex of copper(I) perchlorate. The complex A′ is identical with A, prepared by Hendricker and Bodner. A′ was prepared exactly as Hendricker and Bodner described the preparation of A, and the two compounds have identical ir and uv spectra.

In Table I the theoretical percentages of C, H, N, Cu, and ClO_4^- are given for the formula proposed here and for that proposed by Hendricker and Bodner.

TABLE I

THEORETICAL PERCENTAGES FOR TWO POSSIBLE COPPER PERCHLORATE COMPLEXES

Compd formula	% C	% H	% N	% Cu	% ClO_4^-
$Cu(C_{10}H_{10}N_2)_3(ClO_4)_2$ (A)	48.89	4.10	11.40	8.62	26.99
$Cu(C_{10}H_{10}N_2)_2ClO_4$ (A′)	50.11	4.21	11.69	13.25	20.75

As can be seen from this comparison, C, H, and N analyses are very similar for the two compositions. Copper and perchlorate percentages are very different. Hendricker and Bodner listed only C, H, and N analyses in their paper, so their data are not suitable for distinguishing the two possible formulas. The analyses given below clearly establish this compound as the copper(I) complex $Cu(C_{10}H_{10}N_2)_2ClO_4$.

Since in both of these preparations a copper(I) complex results from a copper(II) starting material, some unexpected reducing agent must be present. This agent appears to be an impurity in the drying agent 2,2′-dimethoxypropane (DMP).

When previously dried starting materials are used and DMP is omitted from the reaction mixture, the copper(I) perchlorate complexes did not form. When a freshly opened bottle of DMP was used instead of a previously opened one, the yield of product was severely reduced. These two observations suggest that some decomposition product of the dimethoxypropane is oxidized by the copper. Ethers are well known to decompose on standing to give a variety of unstable peroxides. Kochi and Mains[2] have investigated the reactions of a number of copper salts with free radicals derived from organic peroxides and found that reduction of copper(II) by these species occurs readily. It therefore seems likely that peroxides arising from slow decomposition of the DMP are responsible for the reduction of copper in this reaction.

The ready preparation of these copper(I) perchlorates suggested that one might be able to prepare other complexes of NN and dmNN directly from copper(I) salts. The brown microcrystalline compounds $Cu_2(NN)Cl_2$ and $Cu_2(dmNN)Cl_2$ have been prepared and characterized as described below.

Preparations. Cu(1,8-naphthyridine)ClO_4 (B).—To a solution of 0.1 g of $Cu(NN)_4(ClO_4)_2$ in 30 ml of absolute methanol, 10 ml of 2,2′-dimethoxypropane was added. The solution was refluxed for 4 hr and then 0.3 g of cupric perchlorate hexahydrate was added. After refluxing for 12 hr more the solution was concentrated by warming under reduced pressure to half its original volume and then placed in a desiccator under nitrogen and over sodium hydroxide. The orange crystals were collected by filtration, washed with chloroform, and dried over calcium chloride. The compound was recrystallized from nitromethane. *Anal.* Calcd for $Cu(C_8H_6N_2)ClO_4$: Cu, 21.67; C, 32.78; H, 2.06. Found: Cu, 21.36; C, 32.67; H, 2.00.

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$Cu(2,7\text{-dimethyl-}1,8\text{-naphthyridine})_2ClO_4$ (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 $Cu(C_{10}H_{10}N_2)_2ClO_4$: 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 $Cu_2(C_8H_6N_2)Cl_2$: 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.

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RECEIVED NOVEMBER 10, 1971

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

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

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

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

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

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

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

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

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