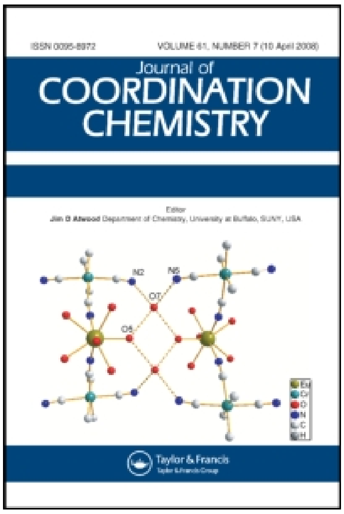

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MAGNETIC BEHAVIOUR OF COPPER(II) AND NICKEL(II) DERIVATIVES OF SUBSTITUTED BENZENEAZO-5-PYRAZOLONES AND -2,4-PENTANEDIONE

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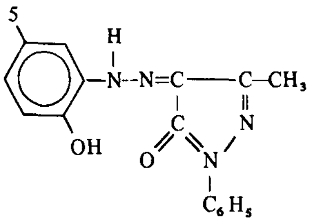
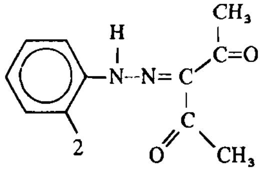
The synthesis and temperature-dependent magnetic properties of copper(II) and nickel(II) complexes of 2-hydroxybenzeneazo derivatives of 1-phenyl-3-methyl-5-pyrazolone and of 2, 4-pentanedione are reported. The copper(II) complexes exhibit antiferromagnetic behavior. It is suggested that these compounds form sheetlike polymers with the copper ion acting as the binding agent between the azo groups and that the antiferromagnetism is due primarily to a direct copper-copper interaction between these sheets. The nickel(II) complexes are diamagnetic which is consistent with the suggested polymer structure.

INTRODUCTION

The magnetic behavior of a number of divalent metal ions with azo derivatives of 5-pyrazolones has been reported.[1] We have recently prepared copper(II) and nickel(II) complexes (1: 1, azo compound to metal) with the *ortho*-hydroxy derivatives of 1-phenyl-3-methyl-4-benzeneazo-5-pyrazolone(I) and 3-benzeneazo-2, 4-pentanedione(II).



(I) 5 = H, Cl or NO_2



(II) 2 = OH or COOH

These compounds have markedly different solubilities and magnetic properties than the previously reported 2:1 metal complexes of simple azopyrazolones.

The stoichiometry for these reactions is:

$$M^{2+} + H_2Ch = MCh + 2H^+$$

where H_2Ch represents the azo compound. The metal compounds often contain either water or ammonia of coordination depending upon the method of preparation.

EXPERIMENTAL

Preparation of Azo Compounds

The azo compounds were prepared in the usual manner. Neutralization equivalents agreed within 0.2% of calculated values.

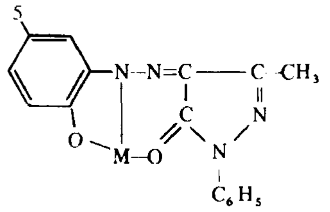
Preparation of Metal Derivatives

Method A. The copper(II) complexes were prepared by dissolving 10 mmol of azo compound in hot 95% ethanol and dioxane (2: 1) to which had been added slightly less than 20 mmol of NaOH. To the hot, filtered solution were added 10 ml of 1M $Cu(NO_3)_2$ dropwise with stirring. The precipitate which formed was digested for about 10 min, suction filtered hot and air dried.

Method B. To a round-bottom flask were added 10 mmol of azo compound, 350 ml of 95% ethanol and 100 ml of conc NH_3. To the boiling solution 10 ml of 1M $Ni(NO_3)_2$ was added at once and the resulting mixture was refluxed on a steam bath for about 5 hours. After cooling, the brown crystals were separated by suction filtration and air dried.

Method C. To 10 mmol of azo compound were added 350 ml of boiling 95% ethanol and 100 ml of conc NH_3. The solution was filtered hot (not quite all of the azo compound dissolved) and 9.5 ml of 1M $Ni(NO_3)_2$, to which had been added 50 ml of conc NH_3, were slowly added with stirring. This solution was evaporated over a steam bath to about

TABLE I
Analytical data for metal derivatives



Azo compound	Metal derivative	% Carbon Cal.	% Carbon Found	% Hydrogen Cal.	% Hydrogen Found	% Nitrogen Cal.	% Nitrogen Found
5-Cl	Cu($C_{16}H_{11}N_4O_2Cl$)	49.24	48.99	2.84	2.86	14.36	14.44
5-NO_2	Cu($C_{16}H_{11}N_5O_4$)	47.94	47.59	2.77	2.81	17.47	17.55
5-H	Ni($C_{16}H_{12}N_4O_2$) · NH_3	52.22	52.43	4.11	4.09	19.03	18.86
5-H	Ni($C_{16}H_{12}N_4O_2$) 1	54.75	54.67	3.45	3.40	15.96	15.81
5-H	Ni($C_{16}H_{12}N_4O_2$) 2	54.75	54.78	3.45	3.42	15.96	15.79
5-H	Ni($C_{16}H_{12}N_4O_2$) 3	54.75	54.90	3.45	3.42	15.96	15.81
2-OH II	Cu($C_{11}H_{10}N_2O_3$)	46.89	46.78	3.57	3.61	9.94	9.68
2-COOH II	Cu($C_{12}H_{10}N_2O_4$)	46.52	47.29	3.43	3.48	9.53	9.06

200 ml. About 50 ml of conc NH_3 were added during the evaporation. Upon cooling, crystals formed which were suction filtered and air dried.

Analysis

Water or ammonia content was obtained by mass loss upon heating to temperatures derived from analysis of DSC curves. Elemental analysis is presented in Table I; analysis by G. Weiler and F. B. Strauss, Oxford, England.

Magnetic Measurements

Magnetic susceptibilities were determined by the Faraday method. A quartz bucket containing about 25 mg of complex was suspended by a copper wire from the arm of a Cahn RG electrobalance into the field of a 4-inch electromagnet equipped with Heyding-type pole faces. The suspension was surrounded by a Pyrex cryostat which housed a copper block to retard cooling. Provision was made to evacuate the cryostat and sample area and to fill with He (0.07 atm) as an exchange gas. Temperature was measured by a copper constantan thermocouple which was affixed to the inside of the cryostat. Liquid nitrogen was used as a refrigerant. The temperature range was 110 to 298°K. The product, HdH/dz, of the nonhomogeneous field produced by the magnet was calculated with Hg[Co(CNS)$_4$] as a standard.[2] Curie-Weiss, $X_M = C/(T + \theta)$, plots were obtained for the paramagnetic species and parameters were determined from a least-squares fit. Molar susceptibilities were corrected for the diamagnetic

TABLE II
Magnetic data for 1:1 Cu(II) complexes

Compound	Magnetic moment (BM)	θ(°K)	g	J(cm^{-1})
Cu(5-H-I)[a]	antiferromagnetic	...	2.06	-206
Cu(5-H-I) · $2NH_3$[b]	1.75	-4	...	...
Cu(5-I)	antiferromagnetic	...	2.10	-180
Cu(5-NO_2-I)	antiferromagnetic	...	2.21	-214
Cu(2-OH-II)	antiferromagnetic	...	2.14	-157
Cu(2-COOH-II)	1.77	-26	...	...

[a] Copper analysis in agreement with calculated value.
[b] By dissolving Cu(5-H-I) in alcoholic ammonia.

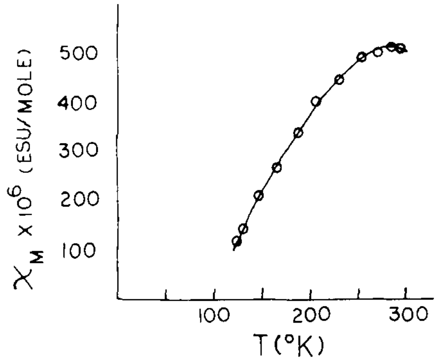


FIGURE 1. The molar magnetic susceptibility (corrected) vs. temperature for the 1:1 copper complex of 1-phenyl-3-methyl-4-(2-hydroxybenzeneazo)-5-pyrazolone.

TABLE III
Magnetic data for nickel(II) complexes of 1-phenyl-3-methyl-4-(2-hydroxybenzeneazo)-5-pyrazolone

Compound	Method of preparation	Magnetic moment (BM)	θ(°K)
Ni(Ch) · $1.8 H_2O$	A	3.15^a	. . .
Ni(Ch) · $3NH_3$	C	3.15	+7
Ni(Ch) · NH_3	B	diamagnetic	. . .
Ni(Ch) – 1^b	–	diamagnetic	. . .
Ni(Ch) – 2^b	–	diamagnetic	. . .
Ni(Ch) – 3^b	–	diamagnetic	. . .

[a] Room temperature measurement.
[b] Obtained from heating Ni(Ch) · $1.8H_2O$ and NiCh · $3NH_3$ to 110 and from NiCh · NH_3 to 195°, respectively.

contributions.[3] A value of 60×10^{-6} cgs/mole was used to correct for the TIP of copper(II).[4]

RESULTS

Copper(II) Complexes

The magnetic behavior of the copper(II) compounds is summarized in Table II. The Cu(5-H-1) · $2NH_3$ gives a moment close to the spin-only value. When the ammonia is driven off, however, the compound exhibits antiferromagnetic behavior as is shown in Figure 1. Similar antiferromagnetic behavior is found for the other copper compounds containing neither ammonia nor water. These compounds, CuCh, are very insoluble in 95% ethanol, benzene, dioxane and other typical solvents. They do dissolve readily in 95% ethanol containing aqueous ammonia and can be isolated as crystalline complexes of the general formula, CuCh · xNH_3. Heating above 110° causes loss of the ammonia, and an antiferromagnetic CuCh is again obtained.

The corrected magnetic susceptibilities for those compounds in Table II exhibiting antiferromagnetic behavior were fitted to the Bleaney-Bowers equation.[5]

$$\chi_{Cu} = \frac{g^2 N\beta^2}{3kT}\left[1 + \frac{1}{3}\exp\left(\frac{-2J}{kT}\right)\right]^{-1}. \qquad (1)$$

The best fit values for g and J are listed in Table II.

The one exception to the above behavior is the copper (II) compound with the 3-(2-COOH-benzeneazo)-2, 4-pentanedione. This copper complex is also insoluble in the above solvents, but it has a moment about that of the spin-only value.

Nickel(II) Complexes

The magnetic behavior of the nickel(II) complexes of 1-phenyl-3-methyl-4-(2-hydroxybenzeneazo)-5-pyrazolone is summarized in Table III. The NiCh · $1.8 H_2O$ and NiCh · $3NH_3$ are paramagnetic and the latter obeys the Curie-Weiss law. When either the water or ammonia is driven off, the compounds are both diamagnetic. The NiCh · NH_3 is diamagnetic. Upon heating to 195°, the ammonia is lost and the resulting NiCh is also diamagnetic. In no case was it possible to prepare the NiCh · NH_3 by careful heating of the NiCh · $3NH_3$ as all the ammonia was lost below 100°C.

DISCUSSION

Copper(II) Compounds

A similar lack of solubility in typical organic solvents of copper(II) complexes of *o*, *o*′-dihydroxyazo dyes is well characterized. It has been suggested that the insolubility of such compounds is due to the formation of sheetlike polymers in which the copper(II) ion serves as the connecting link between dye anions.[6] It was also observed that either ammonia or pyridine was a strong enough ligand to break up the polymer. Soluble monomeric 1:1, metal to dye, complexes were formed which contained either ammonia or pyridine of coordination.

We suggest that the copper(II) complexes, CuCh, in Table II also form sheetlike polymers, Figure 2. Moreover, the observed antiferromagnetic behavior can be explained either through the possible π pathway along the azo bridging group or by direct copper-

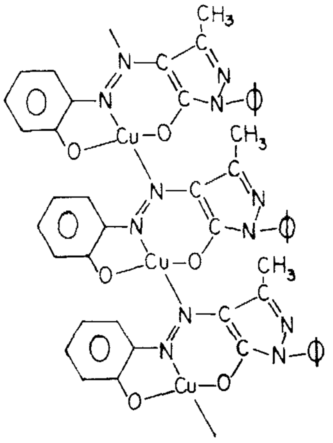


FIGURE 2. Proposed sheetlike polymer for the copper(II) complexes.

copper interaction that can result through the stacking of the sheetlike polymers on top of each other. We prefer the latter explanation for the following reason. The copper(II) complex of the 2-COOH derivative of the azo acetylacetone is paramagnetic. The insolubility of this complex suggests that polymer formation still occurs. Apparently, substitution of the bulkier carboxy group interferes with direct copper-copper bonding between polymer sheets.

The conformity of the magnetic behavior to equation (1), an equation to describe a Cu-Cu dimer interaction, suggests that the copper ions interact in a pairwise fashion. Such an interaction is possible depending on how the polymer sheets are stacked. On the other hand, similar magnetic data has been fitted to equations for tri-, tetra-, and multinuclear interacting complexes.[7,8,9]

Nickel(II) Compounds

The magnetic behavior of the nickel(II) complex, NiCh, can also be explained through polymer formation. Nickel(II) is four coordinate and in a planar environment in the polymer, hence diamagnetic. The NiCh · NH_3 and the NiCh · $3NH_3$ are apparently monomers with the nickel in a planar and octahedral environment, respectively. Whether or not the NiCh · $1.8H_2O$ is a case of 5-coordinate nickel cannot be answered from the above information. It could simply be a case of the polymer in which most of the nickel sites contain two moles of coordinated water, hence 6-coordinated nickel(II).

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