BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 1562—1563 (1973)

Studies on the Interaction between Long Chain Alcohols and Alkyl Sulfates. III. Magnetic Properties of Intermolecular Complexes

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(Received October 19, 1972)

In previous papers, reports were given on the formation of intermolecular complexes between long chain alcohols and metal alkyl sulfates.[1,2] Magnetic properties were examined for the complexes, formed between dodecyl alcohol and dodecyl sulfate, $M(DS)_2$, of divalent metal cations such as Mn^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+} by measuring the electron spin resonance (ESR) and magnetic susceptibility. It is expected that the difference in magnetic property between complex L and complex H, formed above and below the melting point of dodecyl alcohol (25 °C), respectively,[2] can be found by these methods.

Experimental

The apparatus for ESR measurement was a JEOL JES-ME-3X spectrometer of variable-temperature type. Molar ratio of alcohol to sulfate was 6.

Magnetic susceptibilities were measured by Gouy's method. Because of stickiness of the complex it was mixed with NaCl powder (90% wt.) and used as the sample. The specific susceptibility was calculated by Wiedemann's additivity law[3] from the value of the mixed sample:

$$\chi = \chi_1 P_1 + \chi_2 P_2 \cdots\cdots\cdots\cdots\cdots\cdots\cdots \chi_n P_n \qquad (1)$$

where χ is susceptibility of the mixture; χ_n and P_n are susceptibility and weight fraction for the components, respectively. The value of χ_{NaCl} used was -0.515×10^{-6} e.m.u.[4] In order to examine applicability of this dilution method the magnetic susceptibilities of $CuSO_4\cdot5H_2O$ and $M(DS)_2\cdot nH_2O$ were also measured using not only sodium chloride but also naphthalene as a dispersion medium. Since color of the mixture of $CuSO_4\cdot5H_2O$ with NaCl changes with time, the susceptibility was measured just after mixing. Reproducibility was checked by repeating measurement twice for each mixed sample. The result was satisfactory.

Results and Discussion

It is difficult to discuss the electronic state of metals except copper with the results of ESR measurement, since they are in a state of high spin. Thus, only the

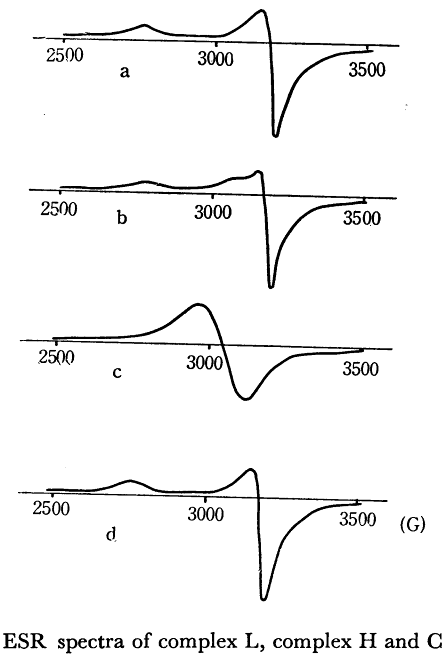

Fig. 1. ESR spectra of complex L, complex H and $Cu(DS)_2\cdot 4H_2O$.
a : complex L (−10°C), b: complex H (28°C),
c : $Cu(DS)_2$ dissolved in DOH (50°C),
d : $Cu(DS)_2\cdot4H_2O$ (28°C)

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[1] Y. Moroi, K. Motomura, and R. Matuura, This Bulletin, **44**, 2078 (1971).

[2] Y. Moroi, K. Motomura, and R. Matuura, *ibid.* **45**, 2697 (1972).

[3] P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., N. Y. (1956), p. 107.

[4] The Chemical Society of Japan, "Kagaku Benran", Maruzen Co., Ltd. (1966), p. 1081.

complex of copper was examined by ESR at various temperatures. The results are shown in Fig. 1. The ESR spectra show hardly any difference between complexes L, H, and $Cu(DS)_2 \cdot 4H_2O$ (a, b, d in Fig. 1). It is evident that the four ligands around the copper atom form a typical square-planar structure. The isotropic pattern at a higher temperature (c in Fig. 1) indicates the dissolution of the complex into DOH.

Table 1. Magnetic susceptibilities and magnetic moments

Sample	Temp. (°C)	$\chi \times 10^6$ (emu)	μ_{eff} (B.M.)
$CuSO_4 \cdot 5H_2O$	25	6.2	1.9
$CuSO_4 \cdot 5H_2O$	25	6.2	1.9
$CuSO_4 \cdot 5H_2O$ (*)	25	5.8	1.9
$Mn(DS)_2 \cdot 6H_2O$	25	19	5.6
$Mn(DS)_2 \cdot 6H_2O$	25	18	5.5
$Mn(DS)_2 \cdot 4DOH$ (L)	20	9.8	5.7
$Mn(DS)_2 \cdot 6DOH$ (H)	35	6.7	5.3
$Co(DS)_2 \cdot 6H_2O$	25	12	4.5
$Co(DS)_2 \cdot 4DOH$ (L)	20	3.0	5.7
$Co(DS)_2 \cdot 6DOH$ (H)	35	4.0	4.2
$Ni(DS)_2 \cdot 6H_2O$	25	5.5	3.0
$Ni(DS)_2 \cdot 4DOH$ (L)	20	6.3	4.6
$Ni(DS)_2 \cdot 6DOH$ (H)	35	1.9	2.6
$Cu(DS)_2 \cdot 4H_2O$	25	1.7	1.6
$Cu(DS)_2 \cdot 4H_2O$ (*)	25	2.3	1.9
$Cu(DS)_2 \cdot 4DOH$ (L)	20	2.0	(2.5)
$Cu(DS)_2 \cdot 6DOH$ (H)	35	1.3	2.1

(*): the dispersing agent is naphthalene.

It is concluded that the alcohol molecules enter the region of metal dodecyl sulfate and form the intermolecular complex with it, the chemical structure around the metal being scarcely changed.

The results of specific susceptibility and magnetic moment are given in Table 1. Since the main object is to detect the difference in chemical state between the complex H and complex L, effective magnetic moment μ_{eff} was calculated by the following equation neglecting diamagnetic term.

$$\mu_{\text{eff}} = \sqrt{\frac{3k\chi T}{N\beta^2}} \quad \text{(B.M.)} \qquad (2)$$

where k is Boltzmann's constant, T absolute temperature, N Avogadro's number and β the Bohr magneton. From the fairly good reproducibility of the results of $CuSO_4 \cdot 5H_2O$ and $Mn(DS)_2 \cdot 6H_2O$, it is evident that a difference exists between the values of μ_{eff} of complexes H and L, which means that they are in different chemical states. Metals except manganese in complex H are more similar in chemical state to those in $M(DS)_2 \cdot nH_2O$ than those in complex L. For manganese, there was little difference in the chemical state between $Mn(DS)_2 \cdot 6H_2O$, $Mn(DS)_2 \cdot 4DOH$ and $Mn(DS)_2 \cdot 6DOH$.

We might conclude that a long chain alcohol infiltrates into the crystal of a metal alkyl sulfate to form a intermolecular complex with the hydroxyl group of the alcohol intermediating. The intermolecular energy was found to be similar in order to that of hydrogen bonding, namely 7—8 kcal/mol-alcohol.[1,2]

The authors wish to express their thanks to Dr. T. Isobe for his kind help and discussion.