Letters to the Editor

Cobaltphenylsiloxane with ferromagnetic interaction

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Polymetallaorganosiloxanes, *i.e.*, the polymers containing fragments RSi—O—M—O— (M = Fe, Co), are paramagnetic.[1] A large number of interatomic metal—metal distances exist in polymeric systems. In this case, the exchange interaction arises in the intrachain and intermolecular coordination clusters of different sizes built of the —M—O—M— fragments. In this work, we studied the metallaorganosiloxane, in which the metal atoms are the constituents of a siloxane framework molecule with definite structural parameters.

Synthesis of cobaltphenylsiloxane was performed by mixing solutions of $[PhSi(ONa)O]_3 \cdot 6C_3H_7OH$ [2] and $CoCl_2$ in *n*-butanol at an equimolar ratio of Na^+ and Cl^-. After removal of precipitated NaCl, the reaction mixture was concentrated, and a crystalline product was obtained. Its recrystallization from a 2 : 1 : 1 Me_2CO—$CHCl_3$—EtOH mixture resulted in a crystalline product of composition $Na\{[PhSiO_2]_6Co_6(\mu_6\text{-}Cl)[O_2SiPh]_6\} \cdot 7Me_2CO \cdot 0.5CHCl_3 \cdot 0.5EtOH \cdot 1.5Bu^nOH$ in 16 % yield. The cage structure[3] of the compound under study is shown in Fig. 1. Removal of the solvate solvents *in vacuo* leads to the destruction of the single crystal; however, crystals with the same unit cell parameters as those of the starting crystalline compound were isolated from the solution of the amorphous compound in a mixture of the above-mentioned solvents. After removal of the solvate solvents, cobaltphenylsiloxane was obtained. Found (%): Co, 17.7; Si, 16.2. Calculated (%): Co, 17.18; Si, 16.37. IR, ν/cm^{-1}: 1130 (Ph—Si); 1050 (Si—O—Si); 950—960 (Si—O—M). UV ($CHCl_3$): λ_{max} = 555 nm, ε = 28.

As can be seen in Fig. 1, in the compound synthesized the Co atoms are united into a metalloxane system by coordination bonds. The possibility of indirect exchange interaction Co^{II}—Co^{II} exists in the metalloxane —Co—O—Co— fragments.

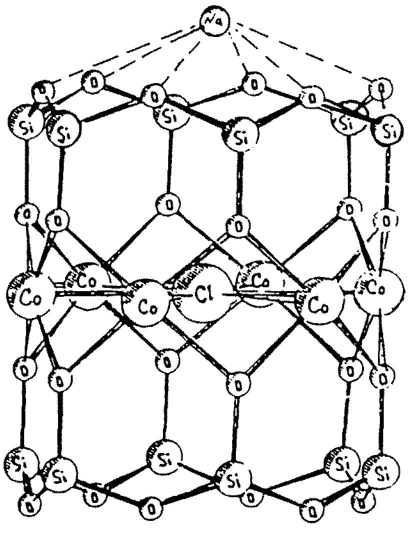

Fig. 1. The structure of the cobaltphenylsiloxane framework (the phenyl groups at the silicon atoms are not shown).

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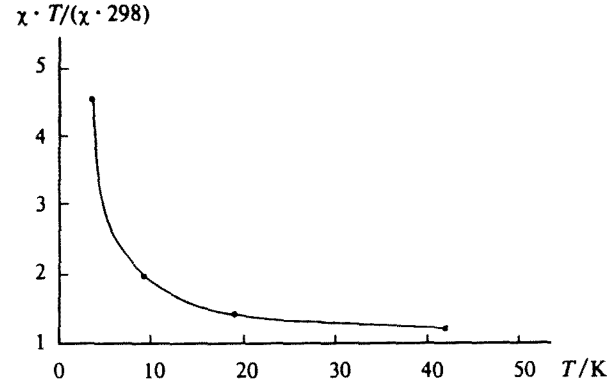

Fig. 2. The temperature dependence of the magnetic susceptibility χ in cobaltphenylsiloxane.

Magnetic measurements were performed on a VSM-155 vibromagnetometer. Temperature dependence of the magnetic susceptibility of cobaltphenylsiloxane is shown in Fig. 2.

Two effects can be mentioned. The first effect is a pronounced deviation from Curie's law. In this case, the ferromagnetic interaction is observed with decreasing temperature which is confirmed by an increase in the effective magnetic moments $\mu_{\rm eff}$ with decreasing temperature: the $\mu_{\rm eff}$ values are equal to 4.05, 5.28, 5.66, 6.91, and 9.20 μ_B at 297, 42.2, 19.4, 9.5, and 4.5 K, respectively (the theoretical value is equal to 3.87 μ_B).

The second effect is the absence of the antiferromagnetic component (*i.e.*, the positive trend of the dependence $\chi \cdot T$ on T). We associate both these effects to the low value of the Co—O—Co angle in cobaltphenylsiloxane. The effect of the —M—O—M— angle on the magnetic behavior was observed previously for Fe complexes.[4] A decrease in the —Fe—O—Fe— angle (due to a change in the nature of the ligand) results in the appearance of ferromagnetic exchange interaction. The value of the Co—O—Co angle, calculated using the published data,[3] is equal to 91.0—92.6°. This value is less than that observed for the known oxo-complexes of Co (102—107° for alkoxy compounds of Co,[5] and 97—98° for siloxy derivatives containing the —Si(R)$_2$—O—Co— fragment[6]).

Thus, the incorporation of Co atoms into a polycyclic siloxane framework results in the disappearance of antiferromagnetic interaction (which is characteristic of complexes of this metal with oxo-ligands) and appearance of ferromagnetic interaction. We believe that the magnetic behavior observed is associated with a specific feature of the structure of the metallosiloxane framework, *viz.*, the reduced value of the Co—O—Co bridge angle.

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Synthesis of tetrasubstituted acylaminophthalocyanines of cobalt

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This work reports a direct template synthesis of tetrasubstituted phthalocyanines of cobalt containing amide groups, which makes it possible to eliminate the stage of formation and isolation of the corresponding phthalogenes.

Reaction (1) occurs in melting of acyl chlorides with anhydrous 4-aminophthalonitrile and CoCl$_2$ (in the ratio 4 : 4 : 1) at 200—210 °C (Wood's alloy bath) for 3 h. The yields of compounds **1a**—**c** amount to 75, 82,

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