

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 μ_{eff} with decreasing temperature: the μ_{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— fragment⁶).

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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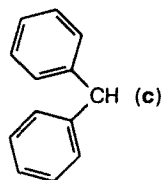
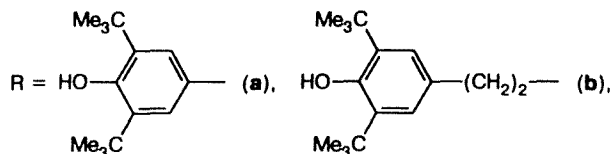
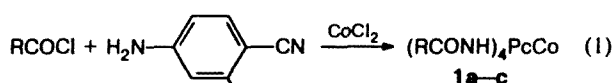
Synthesis of tetrasubstituted acylaminophthalocyanines of cobalt

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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,

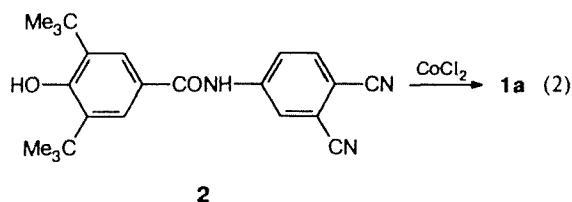


and 79 %, respectively. The products were purified by column chromatography and by thin-layer chromatography on silica gel to obtain analytical samples.

The compounds synthesized are readily soluble in organic solvents. The electronic absorption spectra of compounds **1a–c** in CH_2Cl_2 have Soret bands (330–340 nm), which are typical of metal phthalocyanines and Q-bands in the range of 681, 688, and 675 nm, respectively. A typical absorption spectrum of compound **1b** in DMF is given in Fig. 1.

The IR spectra of compounds **1a–c** have bands in the range of 1690–1700 cm^{-1} (C=O), 3340–3350 cm^{-1} (N–H), and 3630 cm^{-1} (O–H, **1a,b**). The data of elemental analysis correlate satisfactorily with the calculated ones.

Alternatively, compound **1a** was synthesized by reaction of *N*-(3,5-di-*tert*-butyl-4-hydroxybenzoyl)amino-3,4-dicyanobenzene **2** with CoCl_2 (reaction (2)).



Compound **2** was obtained by melting 3,5-di-*tert*-butyl-4-hydroxybenzoyl chloride with 4-aminophthalonitrile in an argon atmosphere at 200 °C (Wood's alloy bath) for 1 h. The yield of product **2** was 82 %. The data of elemental analysis correlate with the calculated ones. M.p. 217–218 °C (from

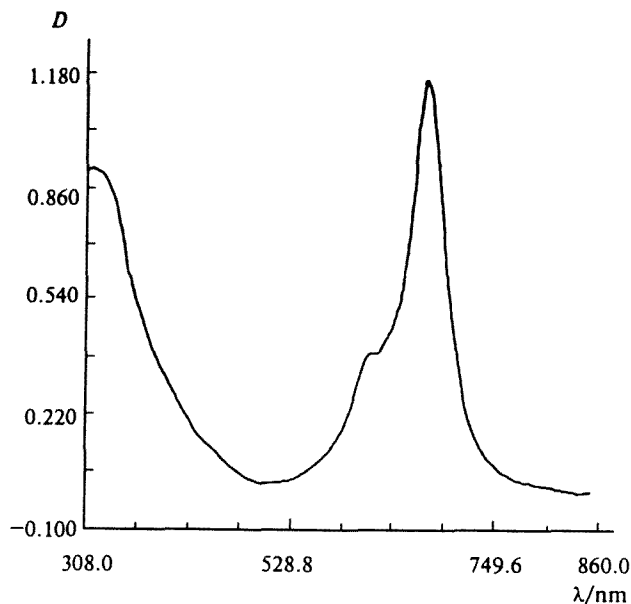


Fig. 1. The absorption spectrum of compound **1b** in DMF ($6 \cdot 10^{-5}$ mol L^{-1}); λ_{max} (Q-band) 682.9 nm, $\log \epsilon$ 4.7019.

MeOH). IR (in pellets with KBr), ν/cm^{-1} : 3635 (O–H); 1700 (C=O); 3350 (N–H). ^1H NMR (CDCl_3), δ : 1.30 (s, 18 H, 6 Me); 5.2 (s, 1 H, OH); 8.9 (s, 1 H, NH); 7.9–8.1 (m, 5 H, arom. ring).

Based on the results obtained with the spectrophotometric monitoring of reaction (1) one can suggest that compounds **1a–c** are formed by sequential acylation of amino groups in cobalt tetraaminophthalocyanine obtained in the first stage, which exhibits a characteristic Q-band in the range of 730 nm,¹ despite possible formation of anilide **2** under these conditions. This suggestion is also confirmed by the data of chromatographic monitoring of the reaction mixtures by TLC on Silufol UV-254 plates.

Esters of the corresponding acids can also be used as acylating agents in the reaction of template synthesis of compounds **1a–c**. However, this leads to a decrease in the yields of the target products.

Reference

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