ing the unpaired electron density in the ligand only in a direction perpendicular to the plane of the latter.

From the magnetic parameters one can calculate the degree of delocalization of the copper ions unpaired electron. The bond coefficient $a^2$ for compounds I-IV was calculated from the Cu(II) hyperfine structure with the approximate formula \[ \alpha^2 = \frac{A^4}{P} + g_1^2 - 2 + 3/7 (g_1 - 2) + 0.04 \]

with $P = 0.036 \text{ cm}^{-1}$, and for compounds V and VI from the hyperfine structure of the nitrogen nuclei and the ligand ($\alpha_N = 14.5 \text{ Oe}$, $\alpha_H = 7 \text{ Oe}$) with the formula for the energy of isotopic interaction of an unpaired electron

\[ W_{N, \text{lig}} = \left( \frac{4\pi}{9} \right) |\bar{\gamma}| \alpha_N \alpha^2 |\bar{\gamma}| N^2 S_f, \]

with normalization

\[ \alpha^2 + \alpha'^2 - 2\alpha' S = 1. \]

The value of the $2\alpha$-function of the ligand $|\bar{\gamma}|_0$ was taken as $33.4 \cdot 10^{-24} \text{ cm}^{-3}$.

The covalency of the metal-ligand bond is a maximum, according to [5], when $a^2 = 0.5$ and a minimum when $a^2 = 1$. For the inner complexes studied $a^2 < 1$ and equal to $\approx 0.78$ in compounds I-IV and $0.72-0.85$ in compounds V-VI, depending on the solvent. This corroborates the presence of a markedly covalent metal-ligand bond in these compounds and agrees with the electron density distribution in them, calculated on the basis of excited states [9]. However, it is difficult to give the comparative covalency of the bonds in all of the above mentioned inner complexes because the covalency of the metal-ligand bond also depends on the nature of the solvent (especially polar solvents). The data from [10] shows the dependence of bond covalency on the environment.

REFERENCES


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I$^{127}$ NQR SPECTRA OF FLUORINATED $\alpha$, $\omega$-DIODOALKANES AND COMPLEXES WITH AMINES

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We have recorded* the NQR spectra of I$^{127}$ ($\pm 1/2$ $\leftrightarrow$ $\pm 3/2$ transition) for certain $\alpha$, $\omega$-diiodofluoroalkanes I(CF$_2$)$_n$I ($n = 2, 4, 6$) and their hydrogen analogs at 77 K (Table 1). The I(CH$_2$)$_n$I series ($n = 1, 2, 4$) gives a frequency gradation as in the corresponding chlorides and bromides [2–4]. The curve with damped oscillations evidently retains its form for small and fairly large $n$: $\nu_{C2} > \nu_{C4} < \nu_{C6}$.

The same gradation is found for I(CF$_2$)$_n$I ($n = 2, 4, 6$): $\nu_{C2} > \nu_{C6} \ll \nu_{C4}$, which is somewhat unexpected. The correlation of reaction constant with NQR frequency indicates [9] that the two should run parallel for I(CF$_2$)$_n$I.

The 1 : 1 complexes of I(CF$_2$)$_n$I with secondary and tertiary amines are also of interest; we have previously [10] examined these for fluorinated halobenzenes. The present complexes are of poor stability, and the method of observation was the steady-state one [8], and we were able to observe the NQR spectrum only of...
The frequency shift of ~6.8 MHz relative to the parent diiodoalkane shows that a charge-transfer complex is produced, which agrees with the result from the UV spectra of fluorinated iodoalkanes [11]. The spectrum of the complex remains of one component (i.e., the two iodine atoms retain their chemical and structural equivalence; this, with considerations of symmetry, indicates a layered structure for the complex in the solid state:

![Diagram of the complex structure](attachment:complex_structure.png)

This screening of the I atoms probably also explains why the I(CF₃)I complexes differ from CF₃ClCFCl(CF₂)nI·N(C₆H₅)₂ in not reacting; the latter are transformed by 40% aqueous NaOH to CF₃CO(CF₂)nI, while reaction with allyl acetate under mild conditions gives CF₃ClCFCl(CF₂)nHH, as we have made previously [12].

These preliminary results show that NQR is a very promising method of examining charge transfer perfluoro complexes.

**EXPERIMENTAL**

The didiiodoperfluoroalkane (0.05 mole) at -80°C was treated with 0.1 mole of diethylamine or triethylamine at the same temperature, which caused a temperature rise of 10-15°C. The reaction mixture was extracted with ether. Distillation of the ether extract gave 4.5 g (45%) of 1-hydro-5,6-dichloropentafluorohexane. Yield 5 g (96.7%), bp 27°C at 15 mm. Found, %: N 1.0. Calculated for C₂₀H₂₄F₁₄I₂N₂, %: N 1.0.

**REFERENCES**

4. I(CF₃)I·N(C₆H₅)₂ (yield 96.7%), bp 27°C at 17 mm, nD₅ 1.4476. Found, %: N 2.89. Calculated for C₂₀H₂₄F₁₄I₂N₂, %: N 2.89.
5. CF₃ClCFCl(CF₃)I·N(C₆H₅)₂ (yield 90%), bp 25°C at 2 mm, nD₃ 1.428, unstable, instantly darkens.
6. CF₃ClCFCl(CF₃)I·N(C₆H₅)₂ (yield 96%), bp 28°C at 0.05 mm, nD₅ 1.393, unstable, becomes dark. Found, %: N 1.6. Calculated for C₆H₅CI₂F₁₄I₂N₂, %: N 1.6.
7. CF₃ClCFCl(CF₃)I·N(C₆H₅)₂ (yield 95%), bp 58°C at 0.08 mm, nD₅ 1.303, unstable. Found, %: C 20.39; H 0.20; F 59.30.

1-Hydro-5,6-dichloropentafluorohexane. A mixture of 18 g of CF₃ClCFCl(CF₃)I·N(C₆H₅)₂ and 0.5 ml of water was heated on a water bath for 3 hr. The product was extracted with ether; the ether solution was washed with hydrochloric acid, sodium bicarbonate, and water, was dried over calcium chloride, and was distilled. Product 2 g (93%) of 1-hydro-5,6-dichloropentafluorohexane, bp 50-52°C at 55 mm, nD₅ 1.4452, light yellow, becomes dark. Found, %: C 21.09, 21.40; H 8.44, 8.37; F 17.88, 17.45; N 8.72, 4.82. Calculated for C₂₀H₂₄F₁₄I₂N₂, %; C 21.09; H 8.29; F 16.70; N 3.07.

1-Hydro-5,6-dichloropentafluorohexane. A mixture of 20 g CF₃ClCFCl(CF₃)I·N(C₆H₅)₂ and 10 ml of 40% caustic soda was heated for 1 hr on the water bath. The product was extracted with ether; the ether solution was washed with hydrochloric acid, sodium bicarbonate, and water, was dried over calcium chloride, and was distilled. Product 3 g (93%) of 1-hydro-5,6-dichloropentafluorobutane, bp 79-80°C at 2 mm, nD₅ 1.3920. Found, %: C 32.92; H 1.65; F 60.53; N 2.70. 1-Hydro-5,6-dichloropentafluorobutane. A mixture of 20 g CF₃ClCFCl(CF₃)I·N(C₆H₅)₂ and 10 ml of 40% caustic soda was heated for 1 hr on the water bath. The product was extracted with ether; the ether solution was washed with hydrochloric acid, sodium bicarbonate, and water, was dried over calcium chloride, and was distilled. Product 3 g (93%) of 1-hydro-5,6-dichloropentafluorobutane, bp 79-80°C at 2 mm, nD₅ 1.3920. Found, %: C 32.92; H 1.65; F 60.53; N 2.70. 1-Hydro-5,6-dichloropentafluorobutane. A mixture of 20 g CF₃ClCFCl(CF₃)I·N(C₆H₅)₂ and 10 ml of 40% caustic soda was heated for 1 hr on the water bath. The product was extracted with ether; the ether solution was washed with hydrochloric acid, sodium bicarbonate, and water, was dried over calcium chloride, and was distilled. Product 3 g (93%) of 1-hydro-5,6-dichloropentafluorobutane, bp 79-80°C at 2 mm, nD₅ 1.3920. Found, %: C 32.92; H 1.65; F 60.53; N 2.70.