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PHOTOCHEMICAL REACTION OF BIS-HALOGENODINITROSYLCOBALT(-I) WITH HEXACARBONYLCHROMIUM(O)

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Photo-induced ligand exchange between $[Co(NO)_2X]_2$ (X = Cl, Br, I) and $[Cr(CO)_6]$ dissolved in THF yields solutions which contain - according to e.s.r. spectra - $[Cr(NO)X_2(THF)_n]$ species. Spin densities, coupling constants, and g values are discussed in the light of varying Cr/X interaction. E.s.r. measurements of the frozen solutions lead to the assumption that g values are anisotropic.

Photoreactions of NO with transition metal carbonyls offer a convenient way for preparing certain nitrosyl complexes (1-3). Comparable reactions occur between nitrosyl complexes and carbonyls. We present here the e.s.r. results of the photoreaction of bis-halogenodinitrosylcobalt(-I) with hexacarbonylchromium(0), which may serve as an example for a more general type of reaction involving halogennitrosyl complexes of cobalt and iron with transition metal carbonyls.

2 mmol of $[Co(NO)_2X]_2$ prepared according to well-known procedures (4) are dissolved together with excess $[Cr(CO)_6]$(appr. 6 mmol) in 400 ml of absol., oxygen-free tetrahydrofuran. The mixture is irradiated for 90 hours at 288 K using a high-pressure mercury source (Hanau TQ 81). According to the spectroscopic data discussed below, the resulting brown (X = Cl, Br) and red (X = I) solutions contain $[Cr(NO)X_2(THF)_n]$. If irradiation is carried out at 210 K, the substances retain CO groups. The solution is evaporated to dryness (during this process, the employed cobalt is almost quantitatively removed in form of $[Co(NO)(CO)_3]$), and the residue is purified by five repricipitations from THF/petrol ether. The elementary analyses of the

substances thus obtained indicate a Cr/N/X ratio different from the species present in solution. The quantities of THF vary; constant conditions during preparation provided, the analytical results were, however, strictly reproducible. E.s.r. spectra of THF solutions (ca. 10^{-3} M) of the isolated compounds are identical with those of the untreated reaction mixtures.

The infrared spectra of the purified substances exhibit a strong and broad ν(NO) band at 1700-1705 cm^{-1} (X = Cl, Br, I), apart from the usual THF bands. E.s.r. spectra were measured in absolute THF solutions under nitrogen atmosphere on a VARIAN V4500 spectrometer equipped with an AEG n.m.r. meter, a HEWLETT-PACKARD 5245L frequency counter, and variable temperature accessory. All manipulations were carried out under nitrogen or using standard high-vacuum-line techniques.

Soon after exposure to u.v., the reaction mixtures show the characteristic e.s.r. spectra. The spectra consist of three lines of equal intensity (X = Cl), or 11 (X = Br) or 13 (X = I) lines, resp., with intensities increasing to the center (cf. Fig. 1). All spectra show satellite quartets of a relative intensity expected for ^{53}Cr. The spectra can be interpreted in terms of the parameters given in Table 1. Hence, the observed spectral pattern is seen to arise from coupling between ^{53}Cr, ^{14}N, and - with the exception of X = Cl (where this coupling is unresolved) - the two equivalent halogen atoms. Simple numerical relations between a(^{14}N) and a(X) reduce the number of lines to those observed.

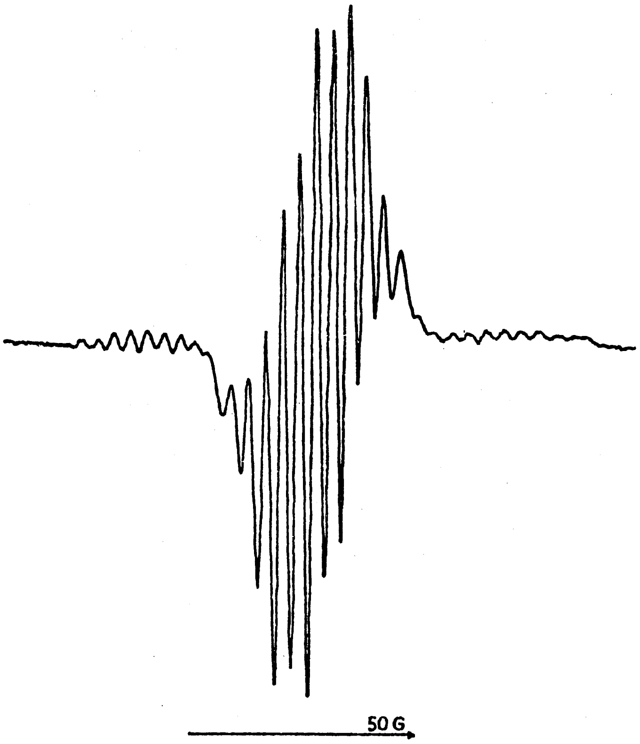

FIGURE 1. E.S.R. Spectrum of [$Cr(NO)Br_2(THF)_n$] at 295 K in THF

TABLE 1

E.S.R. Parameters of [$Cr(NO)X_2(THF)_n$] in THF at 295 K. Spin Densities Calculated with A_o from Ref. (5) in Brackets.

X	g	a(^{14}N)	a(X)	a(^{53}Cr) [G]
Cl	1.9743	6.7 (0.012)	-	22.9 (0.102)
Br	1.9947	6.8 (0.012)	3.4 (0.00042)	22.4 (0.100)
I	2.0178	6.2 (0.011)	6.4 (0.00087)	20.7 (0.092)

The paramagnetic species appear to result from dissociation equilibria: the e.s.r. intensities begin to disappear at about 220 K when the solutions are slowly cooled down, and remain almost constant throughout wide ranges of dilution. However, polycrystalline spectra can be recorded at 150-160 K if the solution is quenched in liquid nitrogen. These spectra (see e.g. Fig. 2) allow to assume that g values are anisotropic. Their partially resolved ligand hyperfine structure could not be assigned unambiguously (cf. Table 2).

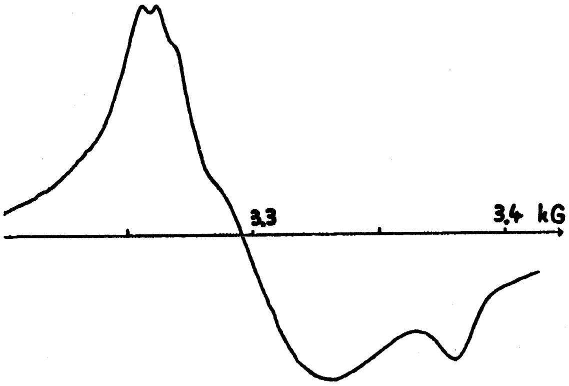

FIGURE 2. E.S.R. Spectrum of [$Cr(NO)Cl_2(THF)_n$] at Approx. 150 K in THF

X	g_1	g_2	g_3
Cl	1.999 (6.0)	1.976 -	1.930 -
Br	2.016 (17.8;8.9)	1.992 -	1.968 -
I	2.034 (14.2;6.6)	2.015 -	1.996 (8.9)

TABLE 2
Anisotropic g values of [$Cr(NO)X_2(THF)_n$] in Frozen THF. Resolved Ligand Couplings [G] in Brackets.

The observed g values, ^{53}Cr, and ^{14}N coupling constants closely resemble those for the well known $[Cr(NO)L_5]^{2+}$ and $[Cr(NO)X(\widehat{LL})_2]^+$ (6,7). In our complexes, the halogen coupling constants clearly indicate that the halogen atoms are directly bonded to the central atom. Thus we may consider the paramagnetic species in solution to be $[Cr(NO)X_2L_n]$ with a still unknown number of THF molecules in the coordination sphere. Consequently, treatment with stronger donors like ethanol or pyridine yields the well known $[Cr(NO)L_5]X_2$ complexes (6,8).

The significant trends of g values, halogen and ^{53}Cr spin densities within the series X = Cl, Br, I provide evidence for an increasing halogen interaction with the ground state. N(s) and Cr(s) functions give considerable contributions to the highest occupied molecular orbital (the ^{53}Cr coupling being interpreted as resulting from contact terms). Moreover, assuming that coupling in the polycrystalline spectra indicates the principal value of a halogen coupling tensor, substantial X(p) contributions have to be taken into account. The g anisotropy is consistent with a non-axial structure.

Thus, the e.s.r. spectra indicate a photoreaction between $[Cr(CO)_6]$ and $[Co(NO)_2X]_2$ which leads to simultaneous exchange of three different types of ligands (σ and π donor X, π acceptor and σ donor CO, strong π acceptor and three electron donor NO) between two central metal atoms. According to e.s.r. spectra obtained immediately after beginning of the reaction, radicals may be considered as primary reaction products. Like in other reactions which involve bis-halogenodinitrosylcobalt or -iron and weakened metal-CO bonds (9) the formation of the thermodynamically stable carbonylnitrosylmetals govern the enthalpy balance.

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