Inorganica Chimica Acta, 20 (1976) L21–L24
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Electron Paramagnetic Resonance Spectra and Electronic Structures of Organobis(dimethylglyoximato)cobalt(IV) Complexes

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(Received July 28, 1976)

We have previously described the one-electron oxidations of organobis(dimethylglyoximato)cobalt (III) compounds [1], $[RCo(DH)_2L]$, where $L = H_2O$, *etc.*, to yield the corresponding paramagnetic radical cations, $[RCo(DH)_2L]^+$. The present communication describes more detailed studies of the EPR spectra of these novel complexes the results of which reveal certain features of their electronic structure. A principal objective of this study was to characterize the distribution of the unpaired electron in these radical cations, particularly with a view to distinguishing between the cobalt atom and the ligands as possible sites of electron removal, *i.e.*, between the limiting configurations, $[Co^{IV}R^-]$ and $[Co^{III}R\cdot]$.

Typical EPR spectra, measured in liquid and frozen solutions, are shown in Figure 1. These reveal the characteristic patterns of eight hyperfine (HF) lines due to the interaction of the unpaired electron with one cobalt nucleus (I = 7/2). The dominant HF structure of the frozen spectra is attributed, on the basis of unambiguous computer simulation [2], to the parallel orientation of the complex in the

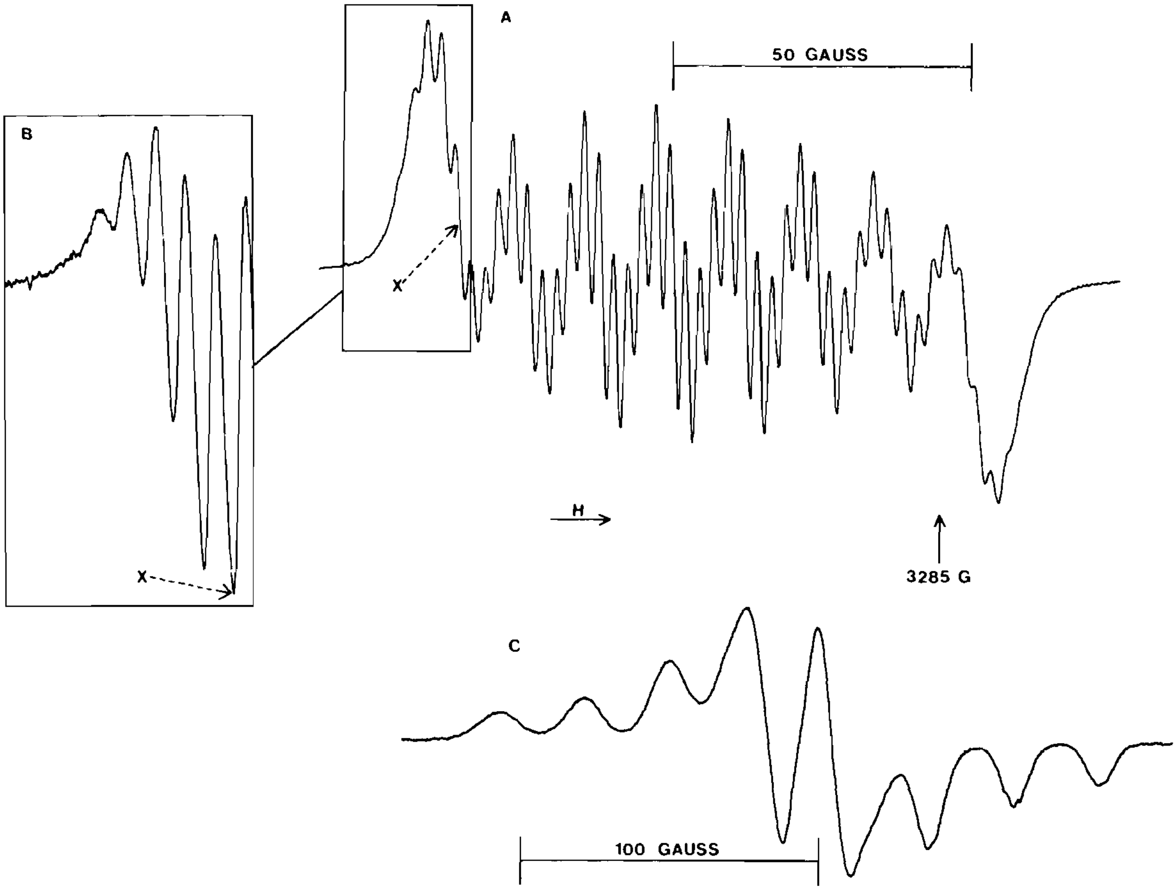

Figure 1. (A) First derivative EPR spectrum of $[C_6H_5Co(DH)_2L]^+$ in CH_2Cl_2 at −30 °C. Microwave frequency is 9.172 GHz. (B) Second derivative EPR spectrum of low field HF component of $[C_6H_5Co(DH)_2L]^+$. X indicates central nitrogen SHF line of this HF component. (C) First derivative EPR spectrum of $[CH_3Co(DH)_2L]^+$ in frozen $CD_3OD:D_2O$ (9:1) at −110 °C. Microwave frequency is 9.170 GHz.

TABLE I. EPR Parameters for $[RCo(DIOXIME)_2L]^+$ Complexes.

R	DIOXIME	g_{iso} (± 0.0003)	$A_{iso}^{Co} \times 10^4$, cm^{-1} (± 0.5)	$g_{\parallel}$ (± 0.002)	$A_{\parallel}^{Co} \times 10^4$, cm^{-1} (± 0.5)	$g_{\perp}$ (± 0.002)	$A_{\perp}^{Co} \times 10^4$, cm^{-1} (± 0.5)
CH_3	DH_2	2.0256[a]	12.9[a]	2.025	29.1	2.026	4.8
CH_3	DPH_2	2.026	11.7	2.028	27.2	2.025	4.0
CH_3	MeO-DPH_2	2.026	12.0	2.027	27.1	2.026	4.5
CH_3CH_2	DH_2	2.0292	13.6	2.031	31.3	2.028	4.8
$CH_3CH_2CH_2$	DH_2	2.0291	13.8	2.031	32.0	2.028	4.7
$(CH_3)_2CH$	DH_2	2.0326	14.3	2.037	34.9	2.030	4.0
p-NO_2-$C_6H_4CH_2$	DH_2	2.0264	13.2	2.024	28.8	2.028	5.4
p-Cl-$C_6H_4CH_2$	DH_2	2.0294	13.5	2.030	30.4	2.029	5.1
p-F-$C_6H_4CH_2$	DH_2	2.0304	13.6	2.031	30.9	2.030	5.0
$C_6H_5CH_2$	DH_2	2.0311	13.5	2.034	31.7	2.030	4.4
p-CH_3-$C_6H_4CH_2$	DH_2	2.0326	13.8	2.036	32.1	2.031	4.7
C_6H_5	DH_2	2.0197	11.8	2.016	24.8	2.022	5.3

[a] Identical isotropic parameters were measured for R = $^{13}CH_3$ and R = CD_3. DH_2 = dimethylglyoxime, DPH_2 = diphenylglyoxime, MeO-DPH_2 = α-4,4′-dimethoxydiphenylglyoxime.

magnetic field. The experimentally determined EPR parameters, g_{iso}, $|A_{iso}^{Co}|$, $g_{\parallel}$ and $|A_{\parallel}^{Co}|$ for various compounds are listed in Table I together with the calculated values of the HF constant, $|A_{\perp}^{Co}| = 1/2(3|A_{iso}^{Co}| - |A_{\parallel}^{Co}|)$ and $g_{\perp} = 1/2(3g_{iso} - g_{\parallel})$.

For R = CH_3 it was established that the g and A parameters are essentially independent of temperature over the range −10° to −50 °C and of solvent (see Experimental). These observations render unlikely any serious differences between the g and A values for the liquid and frozen solutions and thus permit calculation of $|A_{\perp}^{Co}|$ and $g_{\perp}$.

For several of the compounds, *e.g.*, R = CH_3, C_6H_5 and *p*-NO_2-$C_6H_4CH_2$, additional ligand superhyperfine (SHF) structure attributed to interaction of the unpaired electron with nitrogen nuclei of the dimethylglyoxime ligands was observed both in liquid and frozen solution. The best resolved SHF structure was obtained for R = C_6H_5 in CH_2Cl_2 liquid solution (see Figure 1). The low field cobalt HF component of the spectrum clearly shows the nine-line SHF pattern resulting from the interaction of the unpaired electron with four equivalent nitrogen nuclei. In most cases fewer (typically, only the five most intense of the nine) SHF lines were clearly resolved because of overlap of the HF lines. However, computer simulation demonstrated that even in such cases the isotropic spectra could be fitted in detail only by invoking nine SHF lines resulting from interaction with four equivalent nitrogen nuclei.

Attention is directed to the following features of our experimental data: (i) For all the compounds the EPR paramaters are in the range $|A_{iso}^{Co}| = 11.5 \times 10^{-4}$ to 14.5×10^{-4} cm^{-1}, $|A_{\parallel}^{Co}| = 25.0 \times 10^{-4}$ to 35.0×10^{-4} cm^{-1}, $|A_{\perp}^{Co}| = 4.0 \times 10^{-4}$ to 5.5×10^{-4} cm^{-1}, g_{iso} = 2.020 to 2.033, $g_{\parallel}$ = 2.016 to 2.037 and $g_{\perp}$ = 2.022 to 2.031. (ii) The EPR parameters are relatively insensitive to the nature of R. (iii) The EPR parameters, for a given R, are insensitive to the nature of the substituent on the planar dioxime ligand. (iv) The unpaired electron exhibits equivalent interaction with the four nitrogen atoms of the dimethylglyoxime ligand. The nitrogen SHF constants which also are insensitive to the nature of R (R = CH_3, *p*-$NO_2C_6H_4$-CH_2 and C_6H_5) have the values $A_{iso}^{N} = (2.28 \pm 0.05) \times 10^{-4}$ cm^{-1} and $A_{\parallel}^{N} = (2.86 \pm 0.05) \times 10^{-4}$ cm^{-1}. (v) Substitution of R = $^{12}CH_3$ by R = $^{13}CH_3$ resulted in only a slight broadening of the SHF lines in the isotropic spectrum, corresponding to a ^{13}C SHF constant $A_{iso}^{13C} \sim 1$ gauss. The isotropic EPR spectrum for R = CD_3 was identical to that for R = CH_3.

The result (v) demonstrates conclusively that the unpaired electron in $[CH_3Co(DH)_2L]^+$ is not significantly localized on the axial ligand, R, since the value for A_{iso}^{13C} is negligible compared with that expected for the tetrahedral ^{13}C methyl radical ($A_{iso}^{13C} \sim 300$ gauss) [3]. Because of (ii) and (iii) this inference can also be extended to the other $[RCo]^+$ compounds studied. Result (iv) further suggests that the unpaired electron is not extensively localized on the equatorial dioxime ligand. The values of A^N are considerably smaller than those observed for the free dimethylglyoxime radical (A_{iso}^{N} = 31.7 gauss) [4]. Result (iii) also supports this conclusion. Thus it must be concluded that the unpaired electron is predominantly localized on the cobalt atom and that the radical cations are most appropriately described as organocobalt(IV) species.

The EPR data serve to delineate some features of the electronic structure of these cobalt(IV) complexes. Thus, the SHF results, especially (iv) and (v), favor the location of the molecular orbital of the unpaired electron in the equatorial plane. The small values of A^N (*cf.* A^N_{iso} ~ 16 gauss for $Cu(DH)_2$) suggest the π-type $d_{x^2-y^2}$ rather than the σ-type d_{xy} metal orbital.*

At the same time, the isotropic and anisotropic cobalt HF parameters are seen to be consistently smaller than the values (0.01–0.02 cm^{-1}) [5] which are expected from theoretical calculations for a free cobalt ion. The small values of A^{Co}_{iso} can be interpreted in a manner similar to that used to explain the small A^{Co}_{iso} values for various Co(II) complexes [6]. This explanation assumes some 4*s* orbital admixture to the $3d_{x^2-y^2}$ orbital of the unpaired electron, resulting from low symmetry components in the ligand field of cobalt. Contributions to A^{Co}_{iso} from direct *s*-orbital admixture and through spin polarization from *d*-orbitals have opposite signs and thus can partially cancel each other. The unpaired electron density in the 4*s* orbital (ρ_{4s}) which is necessary to account for the observed A^{Co}_{iso} values can be estimated to be ρ_{4s} ~ 0.02 to 0.06.

The small value of $A^{Co}_{\parallel}$ and $A^{Co}_{\perp}$ can be analogously explained by assuming, in addition, an admixture of the $4p_z$ orbital to the $3d_{x^2-y^2}$ unpaired electron orbital. The mixing of the $3d_{x^2-y^2}$ and $4p_z$ orbitals is consistent with the idealized C_{2v} symmetry of $[RCo(DH)_2L]^+$. Since $A^{Co}_{\perp}$ is small A^{Co}_x and A^{Co}_y cannot be resolved. The dipole–dipole contributions to $A^{Co}_{\parallel}$ and $A^{Co}_{\perp}$ from 3*d* and 4*p* orbitals are known to have different signs and thus can offset each other. Estimates based on procedures outlined previously [7, 8] suggest that about 30% of $4p_z$ admixture to the $3d_{x^2-y^2}$ orbital is sufficient to account for the observed cobalt HF parameters. Note that since $A^{Co}_{\parallel}$, $A^{Co}_{\perp} \ll P$ ($P = 2.0023\ g_N\beta_e\beta_N\langle r^{-3}\rangle_{av}$ ~ 0.02 to 0.03 for cobalt in various oxidation states) [9] these estimates are relatively insensitive to the exact choice for the value of P.

The reasons for the unusually small spin–orbital contributions to the g-values ($\Delta g = g - 2.0023$ ~ 0.02) are not entirely obvious. For the low-spin d^5 configuration numerous excited states may contribute to the g-values, rendering difficult a quantitative interpretation of these parameters. The small value for Δg can be partially accounted for by a very strong ligand field splitting in $[RCo(DH)_2L]^+$; however, this factor alone seems insufficient to account for the entire effect. It is of interest to note that, at least for the R = p-X-$C_6H_4CH_2$ series, the g-values increase monotonically with increasing electron donor strength of R; monotonic trends are also observed for $A^{Co}_{\parallel}$. Because a variety of factors contribute to these parameters, a detailed interpretation of these small variations is not warranted.

A principal objective of these studies has been to characterize the radical cations produced by one-electron oxidation of organocobalt(III) compounds, especially with respect to contributions from the two possible limiting electronic structures $[Co^{III}R^{\bullet}]$ and $[Co^{IV}R^-]$. The evidence derived from our EPR measurements clearly supports the latter formulation. Support for this conclusion is also provided by our earlier cyclic voltammetry measurements on the oxidations of a series of *p*-substituted benzylcobalt(III) compounds, $[p\text{-X-}C_6H_4CH_2Co(DH)_2L]$, which yielded a dependence of the equilibrium constant for the reversible one-electron oxidation (*i.e.*, $E_{1/2}/0.059$) on the Hammett substituent constant of X, corresponding to a ρ value of only *ca.* –1.0 [1]; this value is considered too small to be compatible with R^- being the principal site of electron removal, *i.e.*, with formulation of the resulting radical cation as $[Co^{III}R^{\bullet}]$.

Experimental

Solutions were prepared by dissolving either $[RCo(DH)_2(pyridine)]$ or $[RCo(DH)_2(H_2O)]$ in CH_2Cl_2 or in $CD_3OD:D_2O$ solutions containing 0.1 *M* $HClO_4$, and oxidizing to $[RCo(DH)_2L]^+$ with Br_2, PbO_2 or with a stoichiometric amount of cerium(IV) nitrate. The EPR spectra of the resulting solutions, both in the liquid and frozen states, were measured with a Varian E-9 spectrometer equipped with a Varian E-4540 variable temperature unit. Deuteration of the solvent decreased the dipole–dipole interaction of solvent nuclei with the unpaired electron and improved substantially the resolution of the spectra. It was established, at least for the case of R = CH_3, that solvent variation and the alternative procedures for generation of $[RCo(DH)_2L]^+$ described above yielded identical spectra. The concentration of $[RCo(DH)_2L]^+$ was measured by double integration of its frozen solution EPR spectrum using a frozen toluene solution of DPPH as a reference and was found to correspond to about 80% of the initial $[RCo(DH)_2L]$ concentration.

Acknowledgment

We gratefully acknowledge support of this research by the National Institutes of Health (Grant AM-13339) and, under the U.S.–U.S.S.R. Joint Program in Catalysis (KIZ), by the U.S. National Science Foundation and the Academy of Sciences of the U.S.S.R. We are also grateful to Professor Brian Hoffman of Northwestern University for valuable discussions and suggestions.

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*The coordinate system adopted for $[RCo(DH)_2L]^+$ has the z-axis along R–Co–L with the x- and y-axes in the molecular plane bisecting the N–Co–N angles.

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