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ELECTRON SPIN RESONANCE OF $[Co_2(CO)_6(PBu^n_3)_2]^{\dot{-}}$

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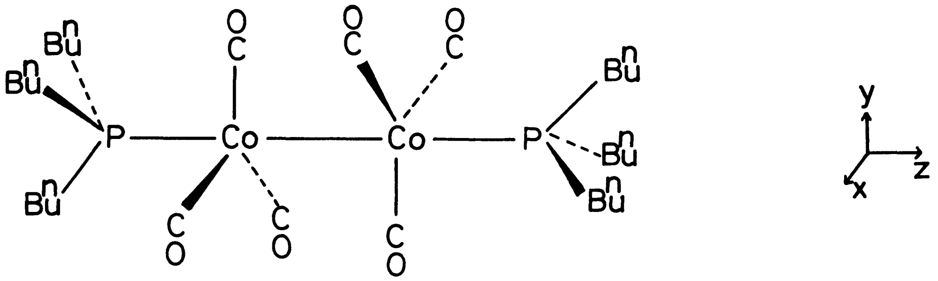
Exposure of a frozen 2-methyltetrahydrofuran solution of $Co_2(CO)_6(PBu^n_3)_2$ to ^{60}Co γ-rays at 77 K gives its anion radical, whose ESR spectrum revealed that the odd electron occupies the orbital mainly of the Co-Co σ^* character together with the Co-P σ^* character ; the orbital consists of 63-65 % cobalt and 23 % phosphorus atomic orbitals.

Electronic structure of metal-metal and metal-ligand bonds in multinuclear transition metal complexes is of current interests.[1] This communication reports the shape of the odd electron orbital of an anion radical, $[Co_2(CO)_6(PBu^n_3)_2]^{\dot{-}}$, deduced from its ESR spectrum.



Irradiation of ^{60}Co γ-rays to a frozen 2-methyltetrahydrofuran (MTHF) solution of $Co_2(CO)_6(PBu^n_3)_2$ at 77 K gave an axially symmetric paramagnetic center containing two magnetically equivalent cobalt nuclei (^{59}Co, I = 7/2, 100 % natural abundance) and two equivalent phosphorus nuclei (^{31}P, I = 1/2, 100 % natural abundance) (Fig. 1). The property of frozen MTHF as a suitable matrix for trapping of anionic species generated by electron attachment to a solute[2] suggests that this radical is the anion of the complex. The validity of this

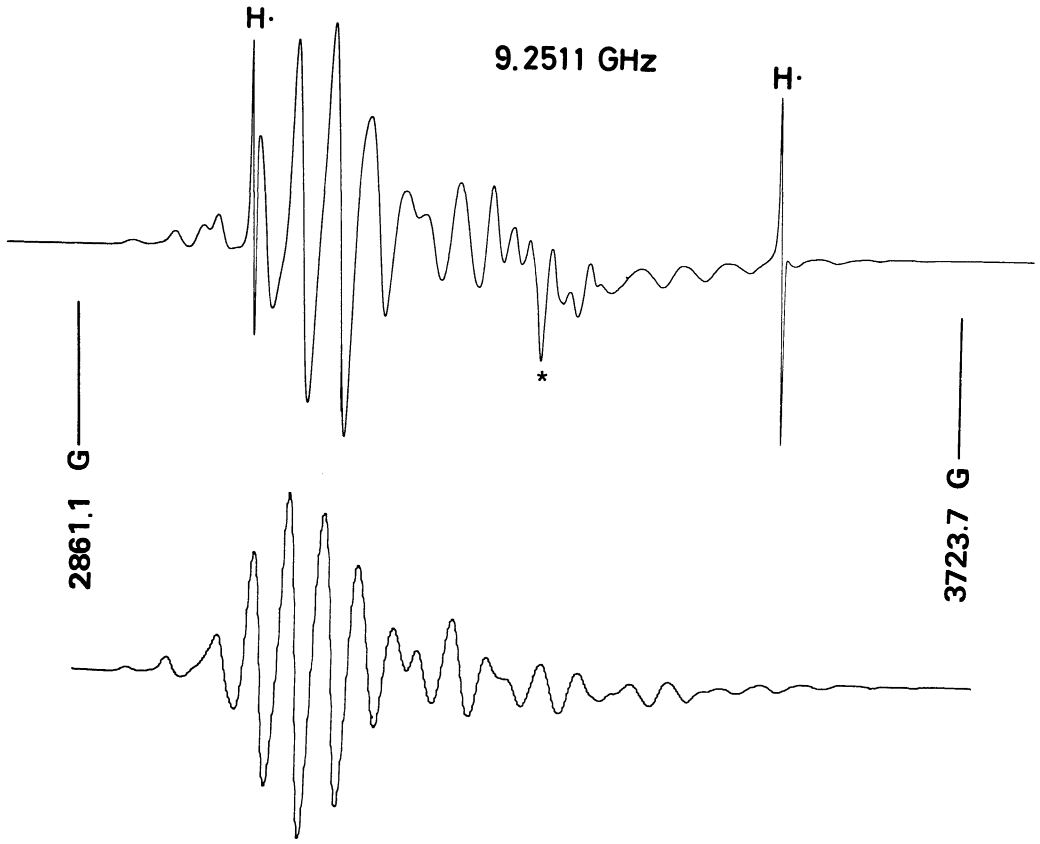


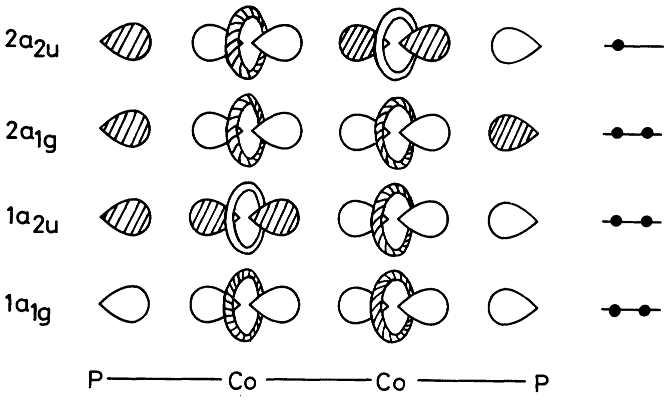
Fig. 1. X-band ESR spectrum of [Co$_2$(CO)$_6$(PBu$^n_3$)$_2$]$^{\dot{-}}$ (77 K). The upper is the observed spectrum and the signal with * is due to an unidentified species. The lower is the simulated one.

electron-gain hypothesis was accomplished by additional experiments. Competitive electron-capture by t-butyl bromide and the complex in MTHF upon γ-radiolysis at 77 K showed that the intensity of ESR absorptions due to t-butyl radical increases at the sacrifice of the signal in Fig. 1 as the concentration of the bromide increases. The spectrum in Fig. 1 is thus attributed to [Co$_2$(CO)$_6$(PBu$^n_3$)$_2$]$^{\dot{-}}$.

The spectrum was analyzed by try-and-error comparison with simulated spectra obtained with second order perturbation treatment of an axially symmetric spin Hamiltonian. ESR parameters derived thereby are as follows: $g_{/\!/} = 2.009_4$, $g_\perp = 2.047_5$, $|A_{/\!/}(\mathrm{Co})| = 38.5 \times 10^{-4}\ \mathrm{cm}^{-1}$, $|A_\perp(\mathrm{Co})| = 29.4 \times 10^{-4}\ \mathrm{cm}^{-1}$, $|A_{/\!/}(\mathrm{P})| = 85.5 \times 10^{-4}\ \mathrm{cm}^{-1}$, and $|A_\perp(\mathrm{P})| = 48.4 \times 10^{-4}\ \mathrm{cm}^{-1}$. Experimental Q-band ESR spectra also coincide well with a simulated spectrum obtained with the same ESR parameters. Although the signs of the cobalt hyperfine tensor components are not established, the most chemically reasonable combination of signs is positive for $A_{/\!/}$(Co) and negative for $A_\perp$(Co). This corresponds uniquely to the odd electron orbital with σ symmetry with respect to the P-Co-Co-P axis (a_{1g} or a_{2u} in D_{3d}).

After appropriate small corrections for second order contribution of unquenched orbital angular momentum of the odd electron (due to large l-s coupling around cobalt atoms) to hyperfine terms,$^{3)}$ the first order Fermi contact and spin dipolar couplings of cobalt nuclei are estimated as a(Co) = -11.0×10^{-4} and 2b(Co) = 50.4×10^{-4} cm^{-1}, respectively. The 2b(Co) value divided by 2B(Co), which is the coupling for unit occupancy of a 3d orbital,$^{4)}$ gives an odd electron density of $\rho(Co, 3d_z2)$ = 0.31 for each cobalt atom. By assuming the contribution of inner shell spin-polarization to a(Co) is proportional to $\rho(Co, 3d_z2)$ with coefficient of ($-94\sim-131$) $\times 10^{-4}$ cm^{-1} $^{1b,5)}$ the odd electron density on a Co 4s orbital is deduced as $\rho(Co, 4s) = 0.009\sim0.015$. The odd electron densities on valence shell atomic orbitals of phosphorus atom were estimated as $\rho(P, 3p_z)$ = 0.10 and $\rho(P, 3s)$ = 0.014 by neglecting inner shell spin-polarization and adopting physically meaningful choice of positive signs for $A_{/\!/}(P)$ and $A_{\perp}(P)$.

The fairly large odd electron density on the phosphorus atoms indicates that the odd electron is delocalized onto the lone pair orbitals on the axial ligands, supporting the former conclusion that the odd electron orbital has σ symmetry with respect to the molecular axis. By referring to a bonding scheme for this complex and fairly large odd electron densities on cobalt and phosphorus



atoms, the odd electron orbital of the present species is reasonably assigned to $2a_{2u}$ orbital with Co-Co $\sigma^{*6)}$ and Co-P σ^* characters. It is thus concluded that the odd electron orbital of $[Co_2(CO)_6(PBu^n_3)_2]^{\dot{-}}$, which would be approximately equal to the lowest unoccupied orbital of the neutral parent molecule, has σ antibonding character for both Co-Co and Co-P bonds and consists of cobalt σ atomic orbitals ($64\sim65$ %, and s character is quite small) and the phosphine lone pair orbitals (23 %).⁷⁾ The distribution of an electron in $2a_{2u}$ orbital of the present species is formally rather similar to that of the valence shell highest π orbital of butadiene suggesting effective mixing of cobalt $3d_z2$ and phosphine lone pair orbitals. Although there is no means to decompose the observed cobalt spin dipolar coupling into $3d_z2$ and $4p_z$ components, the small odd electron density on cobalt 4s orbitals suggests that there may not be appreciable mixing of $4p_z$ orbitals, whose energy levels are located higher than those of cobalt 4s orbitals, into the odd electron orbital either.

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References and Notes

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6) Cf. S. W. Bratt and M. C. R. Symons, J. Chem. Soc. Dalton , (1977) 1314 ; H. B. Abrahamson, C. C. Frazier, D. S. Ginley, H. B. Gray, J. Lilienthal, D. R. Tyler, and M. S. Wrighton, Inorg. Chem., 16, 1554 (1977).

7) We suggest the residual part of the odd electron density to reside in equatorial carbonyl ligands.

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