

EPR and Ligand Field Spectroscopic Investigations on $[\text{Os}^{\text{III}}\text{X}_4\text{pyCO}]^-$ Complexes

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Compounds of type $\text{trans}[\text{Os}^{\text{III}}\text{X}_4\text{pyCO}]^-$ ($\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$) were investigated spectroscopically to characterize the chemical bond in the distorted $\text{Os}(\text{III})$ octahedra. The experimental g -factors and $d-d$ electron transitions lead to negative values for the AOM parameters e_{II} of the CO ligand relative to pyridine. The Π -acceptor ability of the two ligands is shown EPR and ligand field spectroscopically, with partial bonding t_2 orbitals. The spin-orbit coupling parameter of $\text{Os}(\text{III})$ results in $\zeta = 2500 \text{ cm}^{-1}$ ($\text{X} = \text{Cl}^-$) and $\zeta = 1000 \text{ cm}^{-1}$ ($\text{X} = \text{I}^-$).

Introduction

In complexes of type $\text{Os}^{\text{III}}\text{X}_4\text{pyCO}^-$ ($\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$) with trans configured pyridine and CO ligands [1], the central ion Os^{3+} is found in the d^5 low-spin configuration with an approximate C_{4v} symmetry concerning the next neighbour ligand atoms. In octahedral surrounding the lowest d -electron ground state ${}^2\text{T}_2(t_2^5)$ is characterized by an EPR-spectroscopically investigated g -tensor, which is a good marker of changes in molecular structure and bonding in the complex. While for Fe^{3+} and Ru^{3+} the splitting of the ground state by the combined effect of spin orbit coupling and low symmetry ligand fields cannot be spectroscopically identified as $d-d$ electron transition between the split terms, by reason of the larger

spin orbit coupling, for Os^{3+} the possibility to observe such transitions should be increased.

In the following EPR and ligand field spectroscopic investigations will be analyzed on the basis of the ligand field model for transition metal compounds. The calculation of transition energies and g -factors of the ground state multiplet makes it possible to characterize the bonding in the covalent-interacting, tetragonal-distorted Os^{3+} complexes. Thereby the interaction of the ${}^2\text{T}_2$ ground state with the higher excited terms of the d^5 configuration can have some influence on the calculated properties, since in contrast to the 3d-row for 5d-complexes, ligand field effects are comparable in their influence on term splitting with the spin orbit coupling.

Experimental

Samples were kindly supplied by Prof. W. Preetz, University of Kiel, FRG. The remission spectra between 4000 and 25000 cm^{-1} were recorded at room temperature with a PMQ III or in solution (CH_2Cl_2) with a DMR 21 spectrometer (C. Zeiss, Oberkochen). The EPR spectra were taken from a Varian E15 EPR-spectrometer at 35 GHz (300, 77 and 4.2 K) and at 9 GHz (variable temperature between 3.8 and 300 K).

Results and Discussion

Table I shows for different complexes $[\text{Os}^{\text{III}}\text{X}_4\text{LL}]^-$ with trans-configured CO or pyridine ligands

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TABLE I. Experimental g -Factors and Band Positions [($d-d$ transitions (E_1, E_2) and 1. charge transfer (CT) band in kK)] for Complexes of type $[\text{OsX}_4\text{COPy}]^-$ and $[\text{OsBr}_4\text{CO}_2]^-$.^a The parameters Δ_2, ζ (in kK), k and I_1/I_2 are calculated in the isolated ${}^2\text{T}_2$ state; in the last two columns the g -factors are listed as calculated with a complete d^5 basis set and the parameters of the one term model.

	g_{\perp}	g_{\parallel}	E_1	E_2	1. CT	Δ_2	ζ	k	I_1/I_2	g_{\perp}	g_{\parallel}
tr.-Cs[OsCl ₄ COPy]	2.46	1.65	7.7	9.4	>23.0	7.8	2.53	0.84	1.22	2.52	0.99
tr.-TEA[OsCl ₄ COPy]	2.55	1.72	7.5	9.5	>23.0	7.9	2.22	1.05	1.17	2.64	1.01
tr.-TEA[OsBr ₄ COPy]	2.50	1.80	6.8	8.4	>17.0	7.2	1.69	1.12	1.11	2.61	1.22
tr.-TBA[OsBr ₄ (CO) ₂]	2.46	1.81	7.6	9.3	>16.0	8.1	1.86	1.06	1.10	2.56	1.21
tr.-TBA[OsI ₄ COPy]	2.31 ^b	1.93 ^b	5.8	6.6	>11.0	6.1	0.87	1.10	1.03	2.39	1.64
tr.-TBA[OsI ₄ (CO) ₂]	2.32 ^b	1.92 ^b	6.3	7.2	>10.0	6.5	0.98	1.10	1.04	2.41	1.59

^a n-Tetrabutylammonium (TBA⁺), Tetraethylammonium (TEA⁺).

^b Calculated within the ${}^2\text{T}_2$ term.

the experimentally investigated d–d electron transitions, together with the 1. charge transfer band and the g-factors of the powdered samples.

The optical spectra are in good agreement with the results of Greulich and Preetz [1]. From the solution spectra characteristic extinctions of $\epsilon \approx 30\text{--}40$ for the two d–d transitions below 10000 cm^{-1} are deduced. For the 1. charge transfer band $\epsilon > 800$ is found. The intensities of the two d–d transitions are comparable in magnitude according to a rough estimate from line width and extinction. Additionally for $[\text{OsBr}_4\text{COPy}]^-$ and $[\text{OsBr}_4(\text{CO})_2]^-$ only a weak absorption ($\epsilon \approx 10$) at $\approx 12200\text{ cm}^{-1}$ could be detected. EPR spectra are observable at low temperature ($T < 20\text{ K}$) with a line width small enough to resolve the signals. The compound trans-n-tetra-butylammonium (TBA⁺)[OsI₄COPy] shows even at 4.2 K only one broad signal ($\Delta H_{pp} \approx 3000\text{ G}$, $g \approx 2.4$), while for [TBA][OsI₄(CO)₂] no signal at all can be observed. In all compounds investigated g-factors correspond with $g_{\perp} > g_{\parallel}$ to an axial symmetry of the ligands. A small orthorhombic component, $g_x \neq g_y$ can be detected in [TBA][OsBr₄COPy]. The main g-tensors should lie in the plane containing the X atoms and be perpendicular to it. The numerical values of the g-factors correspond to a spin doublet ground state with a tetragonal ligand field component splitting the octahedral ${}^2T_2(t_2^5)$ term (2B_2 and 2E in C_{4v} symmetry). Figure 1 shows the splitting of one d

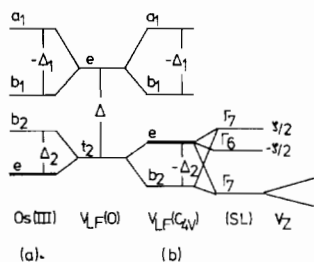


Fig. 1. Term scheme of a d^1 configured cation in octahedral ($V_{LF}(O)$) and tetragonal distorted ligand fields ($V_{LF}(C_{4v})$, compression) with spin orbit coupling (SL) [ξ : spin orbit coupling constant; nondiagonal elements: $\langle (b_2)\Gamma_7 || (SL) || (e)\Gamma_7 \rangle = \xi/\sqrt{2}$] (b) and d^1 term scheme in the special case of Os^{3+} complexes with stronger σ -antibonding and π -bonding axial ligands (a).

state in octahedral symmetry of the ligand field $V_{LF}(O)$ with a tetragonal distortion $V_{LF}(C_{4v})$ including spin orbit coupling. The octahedral e-states are energetically well-separated, and as for (3+)-charged 4d and 5d central ions an octahedral splitting parameter $\Delta > 20000\text{ cm}^{-1}$ is assumed [12]. The parameters Δ_1 and Δ_2 characterize the tetragonal splitting of e and t_2 state, respectively. By definition $\Delta_1, \Delta_2 > 0$ characterizes an elongation along the fourfold axis of the six coordinated complex; ξ describes the effective spin orbit coupling constant.

The Zeeman operator V_z introduces the influence of the external magnetic field into the system.

The transition from one to the five electrons of the Os^{3+} complex leads to the inverted term sequence of the 2T_2 multiplet such that for $\Delta_2, \xi > 0$ the $\Gamma_7(e^4b_2)$ ground state lies below the $\Gamma_7(e^3b_2^2)$ and $\Gamma_6(e^3b_2^3)$ excited states. Only for this arrangement of energy levels can the experimentally-found relation $g_{\perp} > g_{\parallel}$ and two d-electron levels below 10000 cm^{-1} separated by about $\approx 1000\text{--}2000\text{ cm}^{-1}$ be deduced from the model.

To calculate the split parameters from the experimental data we used relations derived for the isolated ${}^2T_2(t_2^5)$ ground state. As the calculated ground state properties can be influenced by the excited states of the d^5 configuration, the g-factors of the complete d^5 configuration are calculated [3] and compared to the results of the one term model (*cf.* Appendix). In an extension of simple relations [5] we get for the one electron transitions in the ${}^2T_2(t_2^5)$ split term system:

$$\Delta E[\Gamma_7(e^4b_2) \longrightarrow \Gamma_7(e^3b_2^2)] = \Delta_2 \cdot S \quad (I_1) \quad (1)$$

$$\Delta E[\Gamma_7(e^4b_2) \longrightarrow \Gamma_6(e^3b_2^2)] = \Delta_2/2(1 + 1.5\eta + S) \quad (I_2) \quad (2)$$

with $\eta = \xi/\Delta_2$ and $S = \sqrt{2\eta^2 + (1 - \eta/2)^2}$. The relative intensities of the two electron transitions can be evaluated on the basis of the 'closure approximation' [4] by the one electron matrix elements $\langle e || p_{\text{eff}}^{xy} || b_2 \rangle$. The ratio of the intensities are derived from:

$$I_1/I_2 = S/2 \frac{(S + 1 - \eta/2)}{(1 - \eta/2)^2} \quad (2)$$

To correct the diagonal matrix elements of the orbital angular momentum in the t_2 orbitals of the $E''(t_2^5)$ ground state for covalency effects an orbital reduction factor k can be introduced [4]. Accordingly the g-factors follow from:

$$g_{\parallel} = 1/S[2 - \eta + k(1 - S - \eta/2)] \quad (3)$$

$$g_{\perp} = 1/S[1 + S - \eta/2 + 2k\eta]$$

The parameters Δ_2, ξ and k calculated with the experimental values from the equations above are collected in Table I. The independently-determined η -values from the optical spectra on the one side and from the g-values on the other are in good agreement with and comparable to those derived from the EPR data of $\text{Os}^{\text{III}}\text{N}_6$ and $\text{Os}^{\text{III}}\text{S}_6$ complex ions [6]. An alternative calculation on the basis of the uncertainty in sign of g-factors results in $\eta > 1$ [6]. This assumption leads to ξ -values far above the empirically derived value for the free Os^{3+} ion ($\xi_0 = 3300\text{ cm}^{-1}$ [2]) and of the ligands ($\xi_0(\text{Cl}^-) = 580\text{ cm}^{-1}$). In addition the intensity I_1 of the lower ligand field transition is calculated from eqn. 2 to be vanishing. The φ -values calculated with (1) show according to

Table I an increasing reduction compared to the φ_0 -value of the free Os^{3+} ion in the sequence $\zeta(\text{Cl}^-) > \zeta(\text{Br}^-) > \zeta(\text{I}^-)$. As in the same direction the spin orbit coupling of the equatorial ligands is strongly increasing, on the basis of molecular orbital considerations [4] this reduction can be attributed to the increasing covalency of the Os–X bond.

The tetragonal splitting parameter Δ_2 of the t_2 states immediately shows the different π -bonding ability of the ligands considered. In the AO model [7] this parameter can be described by

$$\Delta_2 = 2e_\pi(xy) - e_\pi(z) - e_\pi(-z) \quad (4)$$

With the postulated additivity of ligand bonding in this model, one can deduce by comparison of $[\text{OsBr}_4(\text{CO})_2]^-$ and $[\text{OsBr}_4\text{COpy}]^-$ the quantity $e_\pi(\text{CO}) - e_\pi(\text{py}) = -0.9$ kK in agreement with the expected stronger π -acceptor ability of the CO ligand compared to the pyridine molecule. For iodide complexes this difference results in a somewhat smaller but negative value. According to the well-accepted weak π -acceptor ability of the pyridine in 3d complexes [8] ($e_\pi(\text{py}) < 0$) in the Os^{3+} complexes, Δ_2 should be negative and characterizes a tetragonal elongation of the octahedra. This result is far from being trivial, as the axial ligand should be stronger bonded to the central ion compared to the equatorial X atoms which may be visualized by comparison of the bond lengths $\text{Os}^{3+}-\text{Cl}$ (2.36 Å) and Os^+-CO (≈ 1.9 Å) [9] resulting from structure determination. The axial compression of the coordination octahedra, which must be deduced from the structure data, leads to a distortion of the octahedral ${}^2T_2(t_2^5)$ with an orbital singlet ground state corresponding to an elongation in view of axial π -bond strength.

The interaction of the d_{yz} and d_{xz} orbitals with the orbitals of the axial ligands in this model should have bonding character ($e_\pi < 0$) while the equatorial ligands form π -antibonding orbitals ($e_\pi > 0$). In Fig. 1 the special situation in the Os^{3+} complexes considered here is visualized in the sequence of one-electron states. The bond strengths of the equatorial ligands relative to the π -bond of pyridine can be deduced from eqn. 4 with [$e_\pi(\text{CO}) = e_\pi(\text{py}) - 0.9$ kK]: $e_\pi(\text{Cl}) - e_\pi(\text{py}) \approx 3.5$ kK; $e_\pi(\text{Br}) - e_\pi(\text{py}) \approx 3.1$ kK; $e_\pi(\text{I}) - e_\pi(\text{py}) \approx 2.8$ kK with decreasing π -antibonding character in the sequence $\text{Cl} > \text{Br} > \text{I} \gg \text{py} > \text{CO}$. Therefore the negative and positive signs of π -bonding parameters e_π correspond to the concept of π -acceptor and π -antibonding ability of ligands in the AO model.

As g-factors and optical spectra are determined in 1. order only by the π -bonding properties, from the experimental data considered here no information can be deduced concerning the σ -bonding. The absorption at 12.1 kK in the Br complexes depends on at least two additional independent parameters (Δ and Δ_1); therefore no meaningful assignment as

d–d transition and estimation of σ -bonding parameters is possible. The covalency parameters deduced from g-factors are of the order of $k \approx 1$ and are thus of magnitudes comparable to the values found in ionic 3d complexes. As the calculation of g-factors within the complete d^5 -basis shows (*cf.* Appendix), this result is obviously a consequence of the neglect of excited states in the simple ground state model used above. The covalency parameter from eqn. 3 therefore contains all corrections necessary to compensate for the difference between the one term model and the complete configuration interaction model.

In contrast to the g-factors which allow only a rough estimate of the ratio $\eta = \zeta/\Delta_2$ because of their strong dependence on the covalency k , the d–d electron transitions lead directly to the unknown SL coupling constant ζ for Os^{3+} ions in complexes without any remarkable influence of the other excited d^5 configurations. The deduced reduction of ζ from the value ζ_0 of the free ion, $\zeta/\zeta_0 \approx 0.3-0.7$ is comparable to the behaviour found in 3d complexes. The simple ligand field model thus proves as being equally suitable to analyze electronic ground state properties of paramagnetic 5d complexes as in 3d transition metal ions. The applicability of the model to complexes with strong covalent CO ligands may have its origin in the fact that the experimental data considered here are typical ground state properties which depend in 1. order only on metal–ligand π -bonding character.

Appendix

To estimate the influence of the excited d^5 configurations on the 2T_2 ground state multiplet, the g-factors were re-calculated with the parameters of Table I in the strong field coupling scheme with a complete d^5 basis set [3]. For this purpose additional assumptions are necessary to estimate the magnitude of the further parameters of the ligand field model, the octahedral splitting parameter Δ and the Racah parameters B and C. On the basis of empirical data [2] B = 0.4 kK and C = 5B can be fixed. The octahedral Δ parameter is derived from the AO model $\Delta = 3\bar{e}_\sigma - 4\bar{e}_\pi$ (with $e_\pi(\text{py}) = 0$) and the spectrochemical series relation $\Delta = f(\text{ligand}) \cdot g(\text{central ion})$ [10]. With $\Delta([\text{Os}(\text{CN})_6]^{3-}) \approx 38$ kK [2] the parameter values $e_\sigma(\text{Br}) \approx 9.5$ kK and $e_\sigma(\text{py}) \approx 10$ kK lead to $\Delta([\text{OsBr}_4\text{COpy}]^-) \approx 17 + 1/2 e_\sigma(\text{CO})$ kK. As the σ -bonding character of the CO ligand is well established, one can assume $\Delta > 25$ kK. The complete d^5 -basis calculation results in $< 6\%$ contributions of other terms to the ground state ${}^2T_2(t_2^5)$, depending on the magnitude of ζ ($\Delta = 30$ kK, $\Delta_1 = 0$). The calculated g-factors of the last column of Table I show the pronounced dependency of the ground state

Zeeman splitting on the mixing of excited spin and orbital states.

Agreement between experimental g-factors and the calculated properties in the complete configuration scheme can only be achieved if anisotropic orbital reduction factors according to

$$\langle e || \mathbf{1} || e \rangle = k_{\parallel} \langle e(d_{yz}, d_{xz}) || \mathbf{1} || e(d_{yz}, d_{xz}) \rangle$$

$$\langle e || \mathbf{1} || b_2 \rangle = k_{\perp} \langle e(d_{yz}, d_{xz}) || \mathbf{1} || b_2(d_{xy}) \rangle$$

are assumed [3]. The calculated values of $k_{\parallel} \approx 0.2-0.3$ and $k_{\perp} \approx 0.7-0.8$ are found comparable in magnitude to the usual size in 3d transition metal complexes. Despite the possibility to relate the k parameters to bonding properties on the basis of simple MO models [4], the special situation described here proposes them to be treated as pure empirical parameters, e.g. the weak axial π -bonding should lead to $k_{\parallel} > k_{\perp}$, which does not allow to adopt the calculated g-values. The relation $k_{\parallel} \ll k_{\perp}$ can be considered as originating from small, but for the calculated g-factors, important σ -bonding contributions to the ground state by large spin orbit coupling. Consequently, despite the uncommon values of the orbital reduction parameters derived above, the simple 2T_2 model seems to be adequate to relate the

experimental g-factors of low-spin d^5 complexes with the ground state splitting parameters of the ligand field model.

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