tionship between the donor–acceptor properties of ligands and the ability of the complex for oxygen uptake has been determined.

The ability of the examined complexes to carry out electron transfer in catalytic reactions has been studied in the catalytic oxidation of hydrazine and its derivatives with dioxygen.

By means of kinetic methods and EPR measurements the monomeric character of the intermediate complex containing the oxygen molecule and the substrate molecule (both coordinated with cobalt ion) has been established.

The proposed mechanism could be used to explain some catalytic processes involving the contribution of metalloenzymes.

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Molecular Orbital Study of Trimetallic $[M(M'S_4)_2]^{-2}$ Ions $[M = Ni^{II}, Pd^{II}$ or $Pt^{II}; M' = Mo$ or $W]$

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The redox chemistry of sulphur-containing transition metal complexes is of importance in the context of metal–metal bonding as well as biological electron transfer.

In this paper we present the results of our theoretical investigations on Ni, Pd, Pt complexes with tetrathiomolybdate and tetrathiotungstate ions as ligands. These complexes were synthesized for the first time by Müller and co-workers [1] and then by Callahan and Piliero [2]. They have observed that all these compounds undergo novel electrochemical reactions.

For investigations of the electronic structure of trimetallic $[M(M'S_4)_2]^{-n}$ (for various formal oxidation states of the central atom) we have applied two different methods: the extended Hückel method and the parameter-free semiquantitative Frenske–Hall method. The sequence, character and energies of the selected molecular orbitals for $[M(MoS_4)_2]^{-2}$ are presented in Table I (substitution of MoS_4^{-2} by WS_4^{-2} caused no particular changes). The changes in energy of the molecular orbitals and in their composition in dependence on the central atom as well as of the overall charge were discussed. The Mülliken charge analysis was performed. The results achieved by both methods were compared and used for the interpretation of redox properties.

Our calculations indicated significant changes in the character and position of the orbital (LUMO and also the next free one) involved in the electron

TABLE I. Selected Molecular Orbitals of $[M(M'S_4)_2]^{-2}$ Complexes. Energies in eV.

$[Ni(MoS_4)_2]^{-2}$			$[Pd(MoS_4)_2]^{-2}$			$[Pt(MoS_4)_2]^{-2}$		
Orbital	Energy	Character	Orbital	Energy	Character	Orbital	Energy	Character
$4B_{2g}$	-12.990	p_xS_b, $d_{xz}Ni$	$4B_{2g}$	-13.050	p_xS_b, $d_{xz}Pd$	$2A_u$	-12.917	p_yS_b, p_xS_t
$3B_{1g}$	-12.980	$d_{xy}Ni$, p_yS_b	$6B_{1u}$	-12.971	p_zS_b, $d_{x^2-y^2}Mo$	$7A_g$	-12.518	$d_{z^2}Pt$, $d_{x^2-y^2}Pt$
$6B_{1u}$	-12.878	p_zS_b, $d_{x^2-y^2}Mo$	$2A_u$	-12.917	p_yS_b, p_xS_t	$8A_g$	-12.387	$d_{x^2-y^2}Pt$, $d_{z^2}Pt$
$2A_u$	-12.856	p_yS_b, p_xS_t	$3B_{1g}$	-12.836	$d_{xy}Pd$, p_yS_b	$5B_{3g}$	-12.157	$d_{yz}Pt$
$5B_{3g}^*$	-12.804	p_yS_b, $d_{yz}Ni$	$5B_{3g}^*$	-12.754	$d_{yz}Pd$, p_yS_b	$3B_{1g}^*$	-12.149	$d_{xy}Pt$
$5B_{2g}$	-10.941	$d_{xz}Ni$, p_zS_b	$5B_{2g}$	-10.826	$d_{xz}Pd$, p_zS_b	$4B_{1g}$	-10.467	$d_{xy}Mo$, p_xS_t
$4B_{1g}$	-10.529	$d_{xy}Mo$, p_xS_t	$4B_{1g}$	-10.503	$d_{xy}Mo$, p_xS_t	$5B_{2g}$	-10.441	$d_{xz}Pt$, $d_{xz}Mo$
$9A_g$	-10.306	$d_{z^2}Mo$, $d_{z^2}Ni$	$9A_g$	-10.249	$d_{z^2}Mo$, $d_{z^2}Pd$	$3A_u$	-10.220	$d_{xy}Mo$, p_yS_b
$6B_{2u}$	-10.232	$d_{yz}Mo$, $d_{xy}S_b$	$3A_u$	-10.220	$d_{xy}Mo$, p_yS_b	$6B_{2u}$	-10.192	$d_{yz}Mo$, $d_{xy}S_b$
$4B_{3u}$	-10.168	$d_{xz}Mo$, $d_{xy}S_t$	$6B_{2u}$	-10.191	$d_{yz}Mo$, $d_{xy}S_b$	$7B_{1u}$	-10.169	$d_{z^2}Mo$, $d_{z^2}S_t$

*HOMO

transfer process, on going from Ni to Pt along the isoelectron series. These results are in good agreement with electrochemical data [2].

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Metal Complexes of Indolecarboxylic Acids

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Indolecarboxylic acids constitute a well-known class of plant auxins whose biological activity has been related to the formation of stable metal complexes in plant tissues [1]. To establish the nature of the metal–ligand interactions, we are presently investigating binary and ternary complexes formed by natural and synthetic auxins.

We report here preliminary results for the copper(II) complexes of indole-3-acetic acid, indole-3-propionic acid and indole-3-butanoic acid as well as for the copper(II), cobalt(II) and nickel(II) complexes of indole-2-carboxylic acid. The compounds, obtained by reaction of the appropriate acid and metal acetate in aqueous ethanol, have been characterized by means of thermal, spectroscopic and magnetic measurements.

The interaction of copper(II) with indole-3-acetic acid, indole-3-propionic acid and indole-3-butanoic acid yields green complexes having formulae $Cu(IA)_2 \cdot 2H_2O$, $Cu(IP)_2$ and $Cu(IB)_2$*, respectively. Magnetic and ESR data of the complexes are indicative of a structure of the copper(II) acetate type. Also, the solid state electronic spectra are typical of dimeric copper(II) carboxylates through *d–d* absorptions in the 14.5–15.0 kK range and bands at 25.0–26.6 kK characteristic of the bridging system [2].

The complexes of indole-2-carboxylic acid have general formula $M(IC)_2 \cdot 2H_2O$ (M = Ni, Co and Cu). Infrared spectra exclude the involvement of the indole nitrogen in the metal coordination. The electronic spectra of cobalt and nickel complexes agree with a pseudo-octahedral coordination at the metal ion and a donor set of the O_6 type. The copper(II) complex is monomeric. The ESR parameters ($g_\parallel$ = 2.298, $g_\perp$ = 2.106) and electronic data (*d–d* maximum: 14.5 kK) are consistent with a square-planar or strongly distorted tetragonal coordination involving O-donors.

On the whole, all the spectroscopic data indicate that, at least in the solid state, the ligands herein examined act as simple carboxylic acids.

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*Abbreviations: IA, IP, IB and IC denote the deprotonated forms of indole-3-acetic acid, indole-3-propionic acid, indole-3-butanoic acid and indole-2-carboxylic acid, respectively.

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