tion of stability constants from potentiometric titration data: LEAST [1], MINIQUAD [2], MINIQUAD75 [3], MINIQUAD76A [4] and MIQUV [5]. The objective of this research is to develop robust, reliable and fast programs which will enable the solution chemist to specify the composition of any given solution. The last-mentioned program MIQUV was developed to put the model selection process on a sounder statistical basis. Our new program SUPERQUAD is a development of MIQUV designed to be both more efficient and more flexible. The following is a summary of the most important features of the new program.

(1) It uses the method of 'rigorous least squares' in which both e.m.f. (E) and titre values (vol.) are assumed to be subject to experimental error. The data is weighted by a statistically sound weighting scheme. This makes it easier to deal with whole titration curves which include end-points, where measured e.m.f. is very sensitive to variations in volume of titrant added.

(2) The minimization is based on the measured e.m.f. values E_k and all requisite derivatives $\partial E_k/\partial X_j$ are obtained analytically in two stages.

$$\frac{\partial E_k}{\partial X_j} = \frac{\partial E_k}{\partial F_k}\,\frac{\partial F_k}{\partial X_j} \tag{1}$$

$$\sum_k \frac{\partial T_i}{\partial F_k}\,\frac{\partial F_k}{\partial X_j} = \frac{-\partial T_i}{\partial X_j} \tag{2}$$

This approach was first presented by Nagypál [6]. X_j is the jth parameter; it may be a formation constant, a reactant or titrant concentration or a standard electrode potential. Certain parameters may be constrained to be equal. For example the concentration of added alkali can be refined, but constrained to be the same for a set of titration curves. F_k is the kth concentration of free reactant; for example it may be H^+. T_i is the total concentration of the ith reactant.

(3) The statistical information concerning the distribution of weighted residuals on e.m.f. is expected to be most valuable in the process of model selection. Early trials show that the stastical information supplied by SUPERQUAD is more satisfactory than that of MINIQUAD, and leads more convincingly to selection of the best model. In addition to the errors in e.m.f., the errors in volume can also be back-calculated. Thus, the original titration curve can be totally reconstructed, including calculated errors on all measurements.

(4) Flexibility. There may be 1 or 2 electrodes reading either e.m.f. or $-\log F_k$, 2, 3 or 4 reactants and up to 18 formation constants. The case of 2 reactants and 2 electrodes is included. The computer coding (FORTRAN) has been thoroughly checked for portability onto the widest possible range of computers. Input and output have been oriented towards users having 80 characters video display terminals as the principal input/output device.

(5) Details concerning availability of machine-readable copies of SUPERQUAD and associated text data are available from P.G.

1 A. Sabatini and A. Vacca, *J. Chem. Soc. Dalton Trans.*, 1693 (1972).

2 A. Sabatini, A. Vacca and P. Gans, *Talanta, 21,* 53 (1974).

3 P. Gans, A. Sabatini and A. Vacca, *Inorg. Chim. Acta, 18,* 237 (1976).

4 M. Micheloni, A. Sabatini and A. Vacca, *Inorg. Chim. Acta, 25,* 41 (1977).

5 A. Vacca and A. Sabatini, 'MINIQUAD and MIQUV: Two Approaches for the Computation of Stability Constants from Potentiometric Data', in 'Computational Methods for the Determination of Stability Constants', Ed. D. J. Leggett, to be published by Plenum Publ. Corporation, New York.

6 I. Nagypál, I. Paka and L. Zekany, *Talanta, 25,* 549 (1978).

R30

Thermodynamic Electron Transfer and Catalytic Properties of High-Spin Cobalt(II) Complexes with Dioxygen

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The role of high-spin cobalt(II) complexes with bidentate Schiff bases as oxygen carriers in non-aqueous medium has been investigated.

These complexes have the structure of a distorted tetrahedron, both in the solid and in non-coordinating solvents. In the presence of monodentate ligand (amine) they are transformed into pentacoordinated complexes, with their high-spin character preserved. Such a system is capable of reversible, multicycle oxygen uptake at temperatures below 0 °C. The stability constants and thermodynamic values for pentacoordinated complexes have been determined spectrophotometrically. An interesting correlation between the spacial hindrance in the initial complex and the stability constant of the pentacoordinated complex has been found. The monomeric character of the oxygenated complex formed has been established by volumetric, spectrophotometric and EPR methods. Stability constants and the ΔH and ΔS values for the oxygenated complex have been determined for the series of systems. The relationship 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.

R31

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