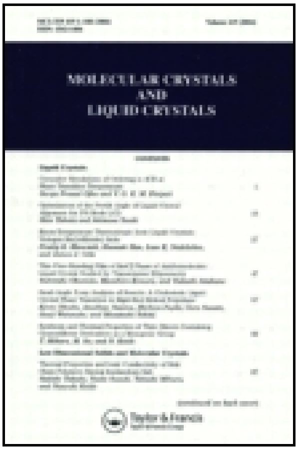

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Application of The MNDO Method for Fe and Mo Compounds

M. Czerwiński [a]

[a] Institute of Chemistry, Pedagogical University, 42-200, Czçstochowa, Poland

To cite this article: M. Czerwiński (1996): Application of The MNDO Method for Fe and Mo Compounds, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 281:1, 171-177

To link to this article: http://dx.doi.org/10.1080/10587259608042242

Mol. Cryst. Liq. Cryst., 1996, Vol. 281, pp. 171–177
Reprints available directly from the publisher
Photocopying permitted by license only

Application of The MNDO Method for Fe and Mo Compounds

M. CZERWIŃSKI

Institute of Chemistry, Pedagogical University, 42-200 Częstochowa, Poland

(Received March 22, 1994; in final form October 20, 1995)

The MNDO SCF-MO treatment has been parametrized for iron and molybdenum. Calculations are reported for a number of compounds. The results of those calculations are comparable with available experimental data.

Keywords: for paper "Application of the MNDO method for Fe and Mo compounds are: MNDO method for transition metals iron and molybdenum; Atomic parameters and parametric functions for two-center integrals of iron and molybdenum.

1. INTRODUCTION

In recent years interest in transition metals has been significantly increasing. Catalysts, biocatalysts and advanced materials studies have spurred this interest. A short list of examples includes Cu in superconductors,[1] Mo and Fe in nitrogenasis, necessary to N_2 reduction,[2] and silver oxide catalysts for the epoxidation of olefins.[3] Investigations elucidating the pertinent electronic structural factors are of interest for materials containing these metals. However, the application of *ab initio* methods to these problems is limited by the large size of many of systems.

The purpose of this work is to examine an approximate molecular orbital method capable of yielding useful information on the electronic structure and geometry of transition metal (Fe and Mo) compounds. The paper describes the MNDO method (one of the variants of the NDDO approximation), which is reasonable in describing the ground state of a variety of transition metal complexes. It has been shown[4–5] that the NDDO method originally proposed by Pople *et al.*[6] yields qualitatively better results than the CNDO or INDO methods. Some problems concerning the choice of one and two electron terms, the parameterization for Fe and Mo, and comparison of results with other calculations and experiments is discussed. The releasing of these parameters gives the possibility of using the MNDO method to study a large system, i.e. molecules, macromolecules, single molecular crystals, and systems including above mentioned metals.

The calculations were carried out using the MOPAC 6.0 package of computer programs.[7] Geometries were optimized by the derivative procedure present in MOPAC using the Broyden-Fletcher-Goldfarb-Shanno method (BFGS).[8–11]

2. DESCRIPTION OF THE MNDO METHOD

The valence shell molecular orbitals (ψ_i) are represented by linear combinations of a minimum basis set of valence shell atomic orbitals (Φ_ν);

$$\psi_i = \sum_{\nu} C_{\nu i}\Phi_\nu. \tag{1}$$

In the MNDO approximation, the differential overlap is neglected only for atomic orbitals on different atoms, e.g., all one-center charge distributions are retained. The matrix elements of the Hartree-Fock operator at this level of approximation and in the closed shell case are:[12, 13]

$$F_{\mu\nu} = H_{\mu\nu} + \sum_{\lambda,\delta}^{A} P_{\lambda\delta}[\langle\mu\nu|\lambda\delta\rangle - 1/2\langle\mu\lambda|\nu\delta\rangle] \tag{2}$$

$$F_{\mu\rho} = H_{\mu\rho} - 1/2\sum_{\nu}^{A}\sum_{\sigma}^{B} P_{\nu\sigma}\langle\mu\nu|\rho\sigma\rangle \tag{3}$$

where μ, ν, λ and δ are centered on atom A, and ρ and σ on atom B. In the open-shell case one has:

$$F^{\alpha}_{\mu\nu} = H_{\mu\nu} + \sum_{\lambda,\delta}^{A} P_{\lambda\delta}[\langle\mu\nu|\lambda\delta\rangle - P^{\alpha}_{\lambda\delta}\langle\mu\lambda|\nu\delta\rangle] \tag{4}$$

$$F^{\alpha}_{\mu\rho} = H_{\mu\rho} - \sum_{\nu}^{A}\sum_{\rho}^{B} P^{\alpha}_{\nu\sigma}\langle\mu\nu|\rho\sigma\rangle \tag{5}$$

where:

$$H_{\mu\nu} = U_{\mu\mu} - \sum_{B(\neq A)} \langle\mu|V_B|\nu\rangle \tag{6}$$

$$H_{\mu\rho} = \beta_{\mu\rho} \tag{7}$$

The elements $F_{\mu\nu}$ of the Fock matrix are the sum of a one-electron part $H_{\mu\nu}$ (core Hamiltonian) and two-electron part $G_{\mu\nu}$ and the electronic energy E_{el} is given by:

$$E_{el} = 1/2\sum_{\mu}\sum_{\nu} P_{\mu\nu}(H_{\mu\nu} + F_{\mu\nu}) \tag{8}$$

where $P_{\mu\nu}$ is an element of the bond order matrix.

The following terms appear in the Fock matrix:

(a) One-center one-electron energies $U_{\mu\mu}$
(b) One-center two-electron repulsion integrals i.e. Coulomb integrals $\langle\mu\mu|\nu\nu\rangle = g_{\mu\nu}$ and exchange integrals $\langle\mu\nu|\mu\nu\rangle = h_{\mu\nu}$
(c) Two-center one-electron core resonance integrals $\beta_{\mu\lambda}$

(d) Two-center one-electron attraction $V_{\mu\nu,B}$
(e) Two-center two-electron repulsion integrals $\langle \mu\nu | \lambda\sigma \rangle$

The total energy E^{mol}_{tot} of the molecule is the sum of the electronic energy E_{el} and the repulsions E^{core}_{AB} between the cores of atoms A and B.

$$E^{mol}_{tot} = E_{el} + \sum_{A<} \sum_{B} E^{core}_{AB}. \qquad (9)$$

The one-center terms $U_{\mu\mu}, g_{\mu\nu}, h_{\mu\nu}$ appear in INDO and MNDO Fock matrixes and can be treated similarly; in both cases these terms are fitted to corresponding spectroscopic values. Two-center repulsion integrals are given as the sum over these semiempirical multipole-multipole interactions:[14-15]

$$\langle \mu\nu | \lambda\delta \rangle = \sum_{l_1} \sum_{l_2} \sum_{m} [M^{\mu\nu}_{l_1 m}(1), M^{\lambda\delta}_{l_2 m}(2)] \qquad (10)$$

where M_{lm} are multipole moments of the two charge distributions, the subscripts l and m specifying the order and orientation of multipoles. The energy interaction between multipoles is calculated by applying an appropriate semiempirical formula:

$$[M^{\mu\nu}_{lm1}, M^{\lambda\delta}_{l2m}] = \frac{e^2}{2^{l_1+l_2}} c^{\mu\nu}_{l_1 m} c^{\lambda\delta}_{l_2 m} \sum_{i=1}^{2^{l_1}} \sum_{j=1}^{2^{l_2}} f_1(R_{ij}) \qquad (11)$$

where R_{ij} is a distance between the point charges i and j, $f_1(R_{ij})$ behaves properly $f_1(R_{AB} \to \infty) = 1/R_{AB}$ and $f_1(R_{AB} \to 0)$ = average value of one-center integrals. For the semiempirical function $f_1(R_{ij})$ in (11), we use the Dewar-Sabelli-Klopman[16-17] (DSK) approximation:

$$f_1(R_{ij}) = [R^2_{ij} + (\rho^{\mu\nu}_{l_1} + \rho^{\lambda\delta}_{l_2})]^{-1/2} \qquad (12)$$

where ρ_l is characteristic for monopole, dipole and quadrupole ($l = 0, 1, 2$) interactions. The core-electron attraction $V_{\mu\nu,B}$ and the core-core repulsions E^{core}_{AB} in semiempirical methods are usually expressed in terms of the two-center repulsion integrals. Early works at the CNDO and INDO level indicated[18-19] that the core-electron attractions are best represented by a Geeppert-Mayer-Sklar (GMS)[20] potential with neglect of penetration integrals in order to avoid a collapse of molecular geometries to extremely short bond lengths. The neglect of penetration integrals decreases absolute values of the core-electron attractions significantly. As a consequence, core-core repulsions must likewise be reduced from their point-charge values $Z_A Z_B e^2 / R_{AB}$ (core charges Z_A and Z_B) in order to keep the balance between the attractions and repulsions in a molecule. The following functions have been investigated for core-electron attraction and the core-core repulsions:

$$V_{\mu\nu,B} = -Z_B \langle \mu^A \nu^A | s^B s^B \rangle, \qquad (13)$$

$$E^{core}_{AB} = Z_A Z_B \langle s^A s^A | s^B s^B \rangle + f_3(R_{AB}), \qquad (14)$$

$$f_3(R_{AB}) = Z_A Z_B \langle s^A s^A | s^B s^B \rangle [\exp(-\alpha_A R_{AB}) + \exp(-\alpha_B R_{AB})]. \qquad (15)$$

The remaining quantities in the MNDO method are one-electron resonance integrals $\beta_{\mu\lambda}$, which provide the main contribution to the bonding energy of a molecule. As in most previous semiempirical methods, they are assumed to be proportional to corresponding overlap integrals $S_{\mu\lambda}$:

$$\beta_{\mu\lambda} = 0.5\,(\beta_\mu + \beta_\lambda) S_{\mu\lambda}. \tag{16}$$

Overlap integrals between the Slater orbitals are evaluated analytically with the orbital exponents being treated as adjustable parameters. Expression (16) also contains adjustable β_μ parameters.

3. PARAMERIZATION PROCEDURE

The determination of parameter values within the MNDO method for Fe and Mo has been carried out for selected compounds, representing various groups from hydrides to oxides, carbonyls, chlorides, metal clusters etc. These compounds contain the elements (without metals) for which parameters of the MNDO method are known. Assuming, after works of Dewar *et al.* [21], we assume that these parameters are unchanged, and describe the calculation of parameters for Fe and Mo. For an element with an *spd* basis there are exactly thirteen parameters i.e. $U_{\mu\mu}, g_{\mu\mu}, \beta_\mu, \zeta_\mu, \alpha$, equal where $\mu = s, p, d.$[15] Our problem is to find optimal values for a set of parameters $X\,(\mu = 1, 2, \ldots)$ towards values of adequate molecular sizes $Y(M = 1, 2, \ldots)$ which are the interatomic distances (angles are frozen) and dipole moment in this case. For $k = \mu$ unknown parameters are determined by solving M non-linear equations.

$$Y_i(X_1, X_2, X_3, \ldots) - Y_{0i} = 0 \quad i = 1, 2, \ldots, M. \tag{17}$$

Practically, these equations are solved by the least squares method. Each parameter Y_i is expanded in the Taylor series around $X_{0\mu}$ neglecting upper elements. The set of parameters $X_{0\mu}(\mu = 1, \ldots, 13)$ has been determined from atomic data i.e. one-center integrals U_{ss}, U_{pp}, U_{dd} have been taken from DiSipio and Tondello[24]. Slater exponents ζ_μ are same as in the paper.[24] Values of the g_{ss}, g_{pp}, g_{dd} integrals, as in case $U_{\mu\mu}$, have been calculated from spectroscopic data.[23] For the resonance integrals β_s and β_p, the assumed values are -1.0, and β_d from paper[22] have been used. During the optimization procedure it was noted that values of parameters which were changing can be limited to parameters U_{dd}, β_d and α, because the remaining parameters depend little on distances between atoms

$$Y_i(X_1, \ldots, X_\mu) = Y_i^0 + \sum_\mu \left(\frac{\partial Y_i}{\partial X_\mu}\right)_0 \Delta X_\mu, \quad \mu = 1, 2, 3; \quad i = 1 \ldots k \tag{18}$$

where: $Y_i^0 = Y(X_{01}, \ldots, X_{0\mu})$, $\Delta X_\mu = X_\mu - X_{0\mu}$. Then the minimization fulfils the following condition:

$$\sum_{i=1}^{M} (Y_{0i} - Y_i^0 - \sum_{\mu=1} B_{i\mu} \Delta X_\mu)^2 = \min \tag{19}$$

where $B_{i\mu} = (\partial Y_i / \partial X_\mu)_0$.

This condition leads to a set of k heterogeneous equations for ΔX_μ values from which we can calculate X_μ. In practice, at $M > \mu$ (in our case $M = 3$) M may by presented in a form of product $M = m * N$, where m is the number of approximate features (interatomic distances and dipole moments), while N is the number of reference molecules for which m features are known. Equilibrium geometries, depending on parameters, have been compared with experimental data. The types of compounds which are used for this scaling calculations restrict usefulness of the results to one-center complexes, compounds, and metal clusters (Tables II, III).

In summary, the following criteria are used in the parameters adjusting procedure:

- be similar to published INDO parameters[22, 23]
- accurately reproduce the experimental bond lengths of sample compounds

TABLE I
MNDO parameters (in eV) for the Fe, Mo elements

Parameters	Fe	Mo
ζ_s	1.35	1.51
ζ_p	1.12	1.24
ζ_d	2.05	1.89
U_{ss}	− 72.60	− 46.43
U_{pp}	− 58.00	− 37.70
U_{dd}	− 96.46	− 40.66
β_s	− 1.00	− 1.00
β_p	− 1.00	− 1.00
β_d	− 24.80	− 21.83
$\alpha(Å^{-1})$	2.00	2.05
g_{ss}	7.38	6.77
g_{pp}	6.10	5.54
g_{dd}	15.37	11.54

TABLE II
Calculated (observed) bond lengths (in Å) for Fe compounds

Compounds	Distance	MNDO	Other calculation	exper.
FeH^*	d(Fe–H)	1.650		1.556 [39]
FeO^*	d(Fe–O)	1.510	1.601 [27]	1.508 [28]
FeF_2	d(Fe–F)	1.890	1.990 [36]	
Fe_4^*	d(Fe–Fe)	2.140	2.280 [37]	
Fe_2	d(Fe–Fe)	2.010		2.020 [31]
$Fe(CO)_5^*$	d(Fe–C)	1.748	1.769 [38]	1.807 [39]
	d(C–O)	1.198	1.157	1.152
FeN_2	d($Fe–N_2$)	2.240	2.290 [32]	
$FeCl_4^{1-}$	d(Fe–Cl)	2.140	2.250 [13]	2.190 [33]
$FeC_6H_5O_3Br^*$	d(Fe–Br)	2.402		2.494 [45]
	d(Fe–O)	2.951		2.934
	d(Fe–C)	2.120		2.120
$FeC_7H_5O_4S^{1+}$	d(Fe–S)	2.140		2.109 [44]
	d(Fe–Cl)	2.110		2.090
	d(Fe–C2)	1.840		1.820
	d(Fe–O)	3.040		3.060

where: d(M–X)—distance of M–X, the angles are frozen.
* denote molecules used in the basis set for parametrization.

- positively influence the convergence of the SCF iteration procedure (less than 200 cycles) (Table III).

Table I presents the adjusted MNDO parameters for the Fe and Mo elements. The results of calculations with these parameters are given in Tables II–IV and these results are compared with the values obtained from other methods.

TABLE III
Calculated (observed) bond lengths (in Å) for Mo compounds

Compounds	Distance	MNDO	Other calculation	experiment
MoH*	d(Mo–H)	1.739	1.743 [34]	
Mo–Mo*	d(Mo–Mo)	1.922		1.938 [35]
MoO_4^{2-}*	d(Mo–O)	1.760	1.784 [40]	1.780 [42]
MoO_2S	d(Mo–S)	2.500		2.532 [29]
	d(Mo–O)	2.200		2.223 [21]
MoO_3S^{2-}	d(Mo–S)	2.150		2.170 [43]
$MoCl_6^{2-}$*	d(Mo–Cl)	2.270		2.310 [30]
MoF_6^{2-}	d(Mo–F)	1.930		1.950 [30]
$MoOCl_4$	d(Mo–O)	1.700	1.690 [38]	1.658 [39]
	d(Mo–Cl)	2.130	2.290	2.279
$Mo(CO)_6$*	d(Mo–C)	2.101		2.063 [41]
$MoC_{10}H_{11}NO_3$	d(Mo–C1)	2.230		2.260 [50]
	d(Mo–C2)	1.950		1.990
	d(C–N)	1.360		1.450
$MoC_{11}H_{11}IO_3$	d(Mo–I)	2.830		2.860 [48]
	d(Mo–O1)	3.110		3.140
	d(Mo–O2)	3.010		3.040
	d(Mo–C1)	1.910		2.000
	d(Mo–C2)	2.360		2.391
$MoC_8H_7I_3O_2$	d(Mo–I)	2.880		2.720 [51]
	d(Mo–O)	3.176		3.010
	d(C–O)	1.120		1.280
$MoC_4H_{10}Cl_2O_4$	d(Mo–O1)	1.630		1.670 [47]
	d(Mo–O2)	2.270		2.290
$MoC_2H_8N_6O_4$	d(Mo–O)	1.740		1.750 [49]
	d(Mo–N1)	3.940		3.930
	d(Mo–N2)	4.190		4.180
	d(Mo–C)	4.530		4.500

where: d(M–X)—distance of M–X

* denote molecules used in the basis set for parametrization.

TABLE IV
Influence of parameters on calculated *d* and μ values (in Å, *D* and *eV*)

α	3.0	2.2	2.0	1.9	1.8	1.0
d(Mo–H)	1.880	1.676	1.715	1.711	1.760	2.210
μ	6.480	6.860	7.010	6.830	7.220	9.440
U_{dd}	−56.60	−54.60	−52.60	−50.60	−48.60	−40.60
d(Mo–H)	XX	1.70	1.69	1.80	XX	1.739
μ	XX	6.53	6.10	7.20	XX	6.35
U_{ss}	−60.43	−48.43	−46.43	−42.00	−40.00	−38.00
d(Mo–H)	1.70	1.70	1.70 SX	XX	XX	XX
μ	6.26	6.47	6.57 SX	XX	XX	XX

where: XX- any convergence; SX- small convergence (convergence after 400 cycles SCF).

The results indicate that the agreement between MNDO and experimental data is quite good.

References

1. J. G. Bednorz, K. A. Muller, *Z. Phys.* **B 64** (1986) 189.
2. R. C. Burns, R. W. F. Hardy, in *Nitrogen fixation in bacteria and higher plants*, Berlin-Heidelberg-New York, Springer 1975 p. 47.
3. K. A. Jorgenesn, *Chem. Rev.* **89** (1989) 431.
4. P. Birner, H. J. Kohler, C. Weiss, *Chem. Phys. Letters*, **27** (1974) 347.
5. W. Thiel, *Theor. Chim. Acta*, **59** (1981) 191.
6. J. A. Pople, D. G. Segal and G. A. Segal, *J. Chem. Phys.*, **43** (1965) 129.
7. J. J. P. Stewart, (1990), Program MOPAC, version 6.0 QCPE no 455.
8. C. G. Broyden, *J. Inst. for Mathem. and Application*, **6** (1970) 222.
9. R. Fletcher, *Comput. J.*, **13** (1970) 317.
10. D. Goldfarb, *Mathem. of Computat.*, **24** (1970) 23.
11. D. F. Shanno, *Mathem. of Computat.*, **24** (1970) 647.
12. M. J. S. Dewar, W. Thiel, *J. Am. Chem. Soc.*, **99** (1977) 4907.
13. Ch. Nicke, J. Reinhold, *Theor. Chim. Acta*, **65** (1984) 91.
14. M. J. S. Dewar, W. Thiel, *Theor. Chim. Acta.*, **46** (1977) 89.
15. W. Thiel, A. A. Voityuk, *Theor. Chim. Acta*, **81** (1992) 391.
16. M. J. S. Dewar, N. L. Hojvat, *J. Chem. Phys.*, **34** (1961) 123.
17. G. Klopman, *J. Am. Chem. Soc.*, **86** (1964) 4550.
18. J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47** (1967) 2026.
19. J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **43** (1965) S 136, **44** (1966) 3289.
20. M. Goeppert-Meyer and A. L. Sklar, *J. Chem. Phys.*, **6** (1938) 645.
21. M. J. S. Dewar, G. L. Grady, and J. J. P. Stewart, *J. Am. Chem. Soc.*, **106** (1984) 6771.
22. A. D. Bacon, M. C. Zerner, *Theor. Chim. Acta*, **53** (1979) 21.
23. W. P. Anderson, T. R. Cundari, M. C. Zerner, *Int. J. Quantum Chem.*, **39** (1991) 31.
24. L. DiSipio, E. Tondello, *Chem. Phys. Lett.*, **11** (1971) 287.
25. E. Tondello, *Inorg. Chim. Acta*, 11 (1974) L5.
26. M. J. S. Dewar and E. Haselbach, *J. Am. Chem. Soc.*, **11** (1970) 590.
27. Ch. W. Bauschlicher, Jr., S. R. Langhoff, A. Komornicki, *Theor. Chim. Acta*, **77** (1990) 263.
28. K. P. Huber, G. Herzberg, *Constants of Diatomic Molecules*, Van Nostrand Reinhold, New York 1979.
29. G. J. Kubas, R. R. Ryan, V. McCarty, *Inorg. Chem.*, **19** (1980) 3003.
30. C. R. Rollinson, *Chromium, Molybdenum and Tungsten. Pergamon Texts in Inorganic Chemistry*, Pergamon Press 1973.
31. H. Purdum, P. Montano, G. Shenoy, T. Morrison, *Phys. Rev. B: Condensed Matter*, **25** (1982) 4412.
32. L. Rincon, F. Ruette, A. Hernandez, *J. Mol. Struct.* (Theochem.), **254** (1992) 39.
33. R. R. Richards, N. W. Gregory, *J. Phys. Chem.*, **63** (1965) 239.
34. C. W. Bauschlicher, C. Nelin, P. Bagus, *J. Chem. Phys.*, **82** (1985) 3265.
35. Y. M. Efremov, A. Samoilova, V. Kozhukhovsky, L. Gurvick, *J. Mol. Spectrosc.*, **73** (1978) 430.
36. B. Rees, A. Mitschler, *J. Am. Chem. Soc.*, **98** (1976) 7918.
37. H. P. Cheng, D. E. Ellis, *J. Chem. Phys.*, **94** (1991) 3735.
38. C. Sosa, J. Andzelm, B. C. Elkin, K. D. Dobbs, D. A. Dixon, *J. Phys. Chem.*, **96** (1992) 6630.
39. K. D. Dobbs, W. J. Hehre, *J. Comput. Chem.*, **8** (1987) 861.
40. B. D. El-Issa, A. A. M. Ali, H. Zanati, *Inorg. Chem.*, **28** (1989) 3297.
41. S. P. Arnesen, H. M. Seip, *Acta Chem. Scand.*, **20** (1966) 2711.
42. F. A. Schroder, *Acta Crystallogr.* Ser. **B, 31** (1975) 2294.
43. H. Schafer, G. Schafer, A. Weiss, Z. Naturforsch., **19B** (1964) 76.
44. G. Hartmann, R. Frobose, R. Mews, G. M. Sheldrick, *Z. Naturforsch.*, **37B** (1982) 1234.
45. F. E. Simon, J. W. Lauher, *Inorg. Chem.*, **19** (1980) 2338.
46. C. F. Putnik, J. J. Welter, G. D. Stucky, *J. Am. Chem. Soc.*, **100** (1978) 4107.
47. B. Kamenar, M. Penavic, B. Korpan-Colig, B. Markovic, *Inorg. Chem. Acta*, **65** (1982) L 245.
48. N. A. Bailey, P. L. Chell, A. Mukhopadhyay, H. E. Tabbron, M. J. Winter, *J. Chem. Soc. Chem. Com.*, **215** (1982).
49. J. R. Dilworth, J. A. Zubieta, *Transition Met. Chem.*, **9** (1984) 39.
50. G. A. Jones, L. J. Guggenberger, *Acta Cryst. Sect.* **B**, 31 (1975) 900.
51. B. S. Erler, J. C. Dewan, S. J. Lippard, D. R. Tyler, *Inorg. Chem.*, **20** (1981) 2719.