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Jahn–Teller Activity of d^x Systems in Tetrahedral Symmetry

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The angular overlap model is used to calculate the Jahn–Teller coupling constants for MX_4 T_d d^x systems in the weak field, $|LSM_LM_S\rangle$, basis. For T states, $T \otimes \epsilon$ coupling most often predominates, but some cases of preferential $T \otimes \tau_2$ coupling are predicted, involving the τ_2 bending rather than the τ_2 stretching mode.

Introduction

The technique of Bacci,[1] for calculating the linear Jahn–Teller coupling constants via the angular overlap model, has been extensively applied to both d^x and f^x systems in O_h symmetry,[2–5] but for T_d species only the results for d^1 and equivalent systems, in the strong-field basis, are available. Moreover, although a strong-field treatment is usually both more natural and quite satisfactory for MX_6 O_h d^x systems,[3] the same cannot be said for the MX_4 T_d 3d complexes, where the ligand field splitting of the d-orbital set is much smaller. Here, when state mixing has to be considered (for $d^2(d^8)$ and $d^3(d^7)$ systems), the values of Δ_{tet} and B (the d-orbital splitting and Racah repulsion parameters) usually encountered lead to states of 95% or greater purity in the weak-field, $|LSM_LM_S\rangle$, basis as against only some 65% in the corresponding strong-field scheme. Consequently, although Bacci's MX_4 T_d values[1,2] apply when the strong- and weak-field results are the same ($d^1(d^9)$ and $d^4(d^6)$ systems), they are not adequate for all d^x configurations. This work now therefore calculates the Jahn–Teller coupling constants for all d^x ground states in T_d symmetry, together with results for the corresponding excited states of the same spin multiplicity, using the weak field, $|LSM_LM_S\rangle$, basis.

Theory

The basis of the angular overlap calculation of the Jahn–Teller coupling constants has been previously presented in several places[1–6] and will not therefore be recapitulated: all the nonvanishing matrix elements of the Jahn–Teller operators were first found in the real d-orbital scheme and converted to the $|m_l\rangle$ basis, and the latter were used to evaluate the general $\langle M_L|\partial V/\partial Q^\Gamma_\gamma|M_L'\rangle$ matrix elements, via the usual operator-equivalent technique. Whereas in O_h symmetry there were but two active modes, ϵ_g (stretching) and τ_{2g} (bending), for T_d species there are now three Jahn–Teller-active vibrations, namely ϵ (δ, bending), τ_2 (δ, bending), and τ_2 (ν, stretching), although, with Bacci,[1] mixing between the two τ_2 modes is for simplicity neglected. The permitted couplings of E and T states to these vibrations are nevertheless the same as in the O_h situation, and the coupling constants, A, B, and C, as defined by Bersuker,[7] and their relationship to E_{JT} are also unaffected.

For $E \otimes \epsilon$ and $T \otimes \epsilon$ the coupling constants A and C, respectively, will be functions simply of e_λ/R, as will the constant B for $T \otimes \tau_2(\delta)$ coupling; for $T \otimes \tau_2(\nu)$ however, B will involve the derivative quantities $\partial e_\lambda/\partial R$. For MX_4 T_d systems the d-orbital set transforms as e + t$_2$, and if only s and p orbitals of the ligands are considered, the e level will be π antibonding and the t$_2$ level both σ and π antibonding. Thus, when the weak- and strong-field results are identical, only e_π terms will occur in the constant A, for E degeneracies, while for T degeneracies both e_σ and e_π quantities arise in B and C. Where state mixing occurs, both e_σ

(1) Bacci, M. *Chem. Phys. Lett.* **1978**, *58*, 537.
(2) Bacci, M. *Chem. Phys.* **1979**, *40*, 237.
(3) Warren, K. D. *Struct. Bonding (Berlin)* **1984**, *57*, 119.
(4) Warren, K. D. *Inorg. Chem.* **1980**, *19*, 653.
(5) Warren, K. D. *Inorg. Chem.* **1982**, *21*, 3467.
(6) Warren, K. D. *Chem. Phys. Lett.* **1982**, *89*, 395.
(7) Bersuker, I. B. *Coord. Chem. Rev.* **1975**, *14*, 357.

Table I. Jahn–Teller Coupling Constants for d^x T_d MX_4 Systems in the Weak-Field Scheme[a]

	d^1, d^6 (d^9, d^4); $^2D, ^5D$
$^{2,5}E \otimes \epsilon$	$A = -(4/3)(2^{1/2}\pi)$
$^{2,5}T_2 \otimes \epsilon$	$C = +(4/3)(2^{1/2}\sigma) - (4/9)(2^{1/2}\pi)$
$^{2,5}T_2 \otimes \tau_2(\delta)$	$B = -(2/3)(2^{1/2}\sigma) + (14/9)(2^{1/2}\pi)$
$^{2,5}T_2 \otimes \tau_2(\nu)$	$B = +(2/3)\dot\sigma - (2/9)\dot\pi$
	d^2, d^7 (d^8, d^3); $^3F, ^4F$
$^{3,4}T_1 \otimes \epsilon$	$C = -(4/5)(2^{1/2}\sigma) + (8/15)(2^{1/2}\pi)$
$^{3,4}T_1 \otimes \tau_2(\delta)$	$B = +(7/5)(2^{1/2}\sigma) - (29/15)(2^{1/2}\pi)$
$^{3,4}T_1 \otimes \tau_2(\nu)$	$B = -(3/5)\dot\sigma + (11/15)\dot\pi$
$^{3,4}T_2 \otimes \epsilon$	$C = +(4/3)(2^{1/2}\sigma) - (16/9)(2^{1/2}\pi)$
$^{3,4}T_2 \otimes \tau_2(\delta)$	$B = +(1/3)(2^{1/2}\sigma) - (7/9)(2^{1/2}\pi)$
$^{3,4}T_2 \otimes \tau_2(\nu)$	$B = -(1/3)\dot\sigma + (1/9)\dot\pi$
	d^2, d^7 (d^8, d^3); $^3P, ^4P$
$^{3,4}T_1 \otimes \epsilon$	$C = +(4/5)(2^{1/2}(\sigma + \pi))$
$^{3,4}T_1 \otimes \tau_2(\delta)$	$B = -(2/5)(2^{1/2}(\sigma + \pi))$
$^{3,4}T_1 \otimes \tau_2(\nu)$	$B = -(2/5)(\dot\sigma + \dot\pi)$

Off-Diagonal Matrix Elements: d^2, d^7 (d^8, d^3); $^3F-^3P$, $^4F-^4P$
$\langle^{3,4}F, 0|\partial V/\partial Q_{z^2}|^{3,4}P, 0\rangle = +(16/15)(2^{1/2}\sigma) + (8/45)(2^{1/2}\pi)$
$\langle^{3,4}F, \pm1|\partial V/\partial Q_{xy}|^{3,4}P, \mp1\rangle$ (δ) $= \pm(7/15)(2^{1/2}i\sigma) \mp (4/45)(2^{1/2}i\pi)$
$\langle^{3,4}F, \pm1|\partial V/\partial Q_{xy}|^{3,4}P, \mp1\rangle$ (ν) $= \pm(2/15)i\dot\sigma \pm (16/45)i\dot\pi$

[a] Here and throughout, $\sigma = e_\sigma/R$, $\pi = e_\pi/R$, $\dot\sigma = \partial e_\sigma/\partial R$, and $\dot\pi = \partial e_\pi/\partial R$. Reverse signs are for hole-equivalent configurations. Allowance for state mixing may be made via the listed off-diagonal matrix elements; note that all elements containing i are Hermitian and make appropriate sign changes for hole-equivalent configurations.

and e_π terms are involved in all the weak-field-scheme coupling constants.

The required calculation for any d^x state may then most readily be made via the operator-equivalent technique by following the procedure used[3] for the MX_6 O_h case. Thus one writes

$$\partial V/\partial Q_{z^2} = \alpha_{0\lambda}O_2^0 + \beta_{0\lambda}(O_4^0 - 7O_4^4)$$

$$\partial V/\partial Q_{x^2-y^2} = \alpha_{2\lambda}O_2^0 + \beta_{2\lambda}O_4^2$$

$$\partial V/\partial Q_{xy} = \alpha_{2\lambda}O_2^0 + \beta_{2\lambda}O_4^2$$

where the O_m^n are the Stevens[8] operator equivalents. The coefficients may then easily be expressed[3,6] in terms of Stevens' α and β quantities, and for the ϵ mode one finds

$$\alpha_{0\sigma} = -2^{1/2}\alpha \qquad \beta_{0\sigma} = +2^{1/2}\beta/2^2 \qquad \alpha_{2\sigma} = +6^{1/2}\alpha$$
$$\beta_{2\sigma} = +6^{1/2}\beta$$

while for the $\tau_2(\delta)$ and $\tau_2(\nu)$ modes, respectively, the results

$$\alpha_{2\sigma} = -2^{1/2}i\alpha \qquad \beta_{2\sigma} = +5(2^{1/2}i\beta/2) \qquad (\delta)$$

and

$$\alpha_{2\sigma} = -i\alpha \qquad \beta_{2\sigma} = -i\beta \qquad (\nu)$$

are derived. The $\alpha_{n\pi}$ and $\beta_{n\pi}$ quantities are simply related to the $\alpha_{n\sigma}$ and $\beta_{n\sigma}$ terms such that in each case $\alpha_{n\pi}/\alpha_{n\sigma} = +1$ and $\beta_{n\pi}/\beta_{n\sigma}$

(8) Stevens, K. W. H. *Proc. Phys. Soc. London, Sec. A* **1952**, *65*, 209.

$= -4/3$. Thus, all the general $\langle M_L |\partial V/\partial Q_\gamma{}^\Gamma| M_L'\rangle$ matrix elements may be found for any E or $T_{1,2}$ state by using the cubic wave functions of Griffith[9] and the appropriate A, B, and C coupling constants deduced.

Results and Discussion

In Table I are listed the Jahn–Teller coupling constants for MX_4 T_d d^x systems ($x = 1–4, 6–9$), in the weak-field basis; the $^6A_1$ d^5 state is of course Jahn–Teller impotent. Results are given for the ground states and for excited states of the same spin multiplicity, and where state mixing occurs, allowance may, if desired, be made for this usually small effect by using the listed cross-product matrix elements.

According to the angular overlap approach, the d-orbital splittings, Δ_{oct} ($=E(e_g) - E(t_{2g})$) for MX_6 systems and Δ_{tet} ($=E(e) - E(t_2)$) for MX_4 systems, are given by $\Delta_{oct} = 3e_\sigma - 4e_\pi$ and $\Delta_{tet} = -(4/3)e_\sigma + (16/9)e_\pi$, respectively, although in practice, the ratio $-\Delta_{tet}/\Delta_{oct}$ is often slightly greater than the predicted factor of $^4/_9$. Nevertheless, the much reduced splitting leads always to high-spin ground states of high weak-field purity. Since however only the single parameter Δ is experimentally available, evaluation of the e_λ requires the determination of the e_π/e_σ ratio, which angular overlap theory indicates should be equal to $(S_\pi{}^2/S_\sigma{}^2)$, where the S_λ terms are the respective group overlap integrals. Such calculations suggest a ratio of about 0.25, but since empirical data for lower symmetry species yield rather smaller ratios, E_{JT} is here determined assuming e_π/e_σ to range between about $^1/_6$ and $^1/_4$.

For O_h MX_6 systems the e_g orbitals are markedly σ antibonding whereas the t_{2g} set interacts only in a π sense: much larger E_{JT} values are therefore anticipated for E than for T states, and thus little attention has been given to the relative strengths of T $\otimes$ ϵ_g and T $\otimes$ τ_{2g} coupling. For T_d MX_4 species however, the converse situation obtains so that E_{JT} for E states will be rather small and significantly greater values should arise for T levels. Consequently, the competition between T $\otimes$ ϵ and T $\otimes$ τ_2 coupling assumes much greater significance, as well as the possible conflict between the $\tau_2(\delta)$ and $\tau_2(\nu)$ modes, and for the latter the simple electrostatic model relationship, $\partial e_\lambda/\partial R = -5e_\lambda/R$, was assumed in calculating E_{JT}.

For the 3d series approximately tetrahedral $[MCl_4]^{2-}$ complexes are known for M = Mn, Fe, Co, Ni, and Cu (d^5–d^9), of which only the Cu compound is substantially distorted from T_d symmetry. In Table II are given the corresponding E_{JT} values, calculated from the cited experimental data, showing coupling of the various T states to the ϵ mode to be dominant in most cases and very strong for $^2T_2$ of $[CuCl_4]^{2-}$. In two instances however—the $^3T_1(F)$ and $^4T_1(F)$ states of $[NiCl_4]^{2-}$ and $[CoCl_4]^{2-}$—the calculated $E_{JT}/\hbar\omega$ ratio suggests that T $\otimes$ $\tau_2(\nu)$ coupling should be favored, although in no case is T $\otimes$ $\tau_2(\nu)$ predicted to be the strongest. Of the above anions, those of Mn, Fe, Co, and Ni show a very nearly T_d geometry,[10-12] with only slight tetragonal distortions toward D_{2d} symmetry, but since the d^5 Mn^{II} and d^7 Co^{II} complexes have essentially Jahn–Teller-inactive $^6A_1$ and $^4A_2$ ground states, respectively, it is very unlikely that these small distortions are of Jahn–Teller origin.

The d^9 $[CuCl_4]^{2-}$ anion is however substantially distorted from T_d toward D_{2d} symmetry,[13,14] as would be expepcted for the strong $^2T_2$ $\otimes$ ϵ coupling. Here $E_{JT}/\hbar\omega$ is large enough to stabilize a static distortion despite the appreciable spin–orbit coupling (ξ for Cu^{II} is[9] 930 cm^{-1}), which splits $^2T_2$ into $\Gamma_7 + \Gamma_8$ with the former lying lower. Thus, despite the Jahn–Teller impotence of an isolated Γ_7 Kramers' doublet, the very strong coupling acts via the matrix elements connecting Γ_7 and Γ_8, thereby stabilizing the distorted configurations. In fact, Bacci's data[15] predict a comparable E_{JT}

(9) Griffith, J. S. *The Theory of Transition Metal Ions*; Cambridge University Press: London, 1964.
(10) Figgis, B. N.; Gerloch, M.; Mason, R. *Acta Crystallogr.* **1964**, *17*, 506.
(11) Stucky, G. B.; Folkers, J. B.; Kistenmacher, T. J. *Acta Crystallogr.* **1967**, *23*, 1064.
(12) Pauling, P. *Inorg. Chem.* **1966**, *5*, 1498.
(13) Helmholz, L.; Kruh, R. F. *J. Am. Chem. Soc.* **1952**, *74*, 1176.
(14) Morosin, B.; Lingafelter, E. C. *J. Phys. Chem.* **1961**, *65*, 50.

Table II. Jahn–Teller Stabilization Energies for d^x ($x = 6–9$) $[MCl_4]^{2-}$ Anions[a]

	E_{JT}, cm^{-1}	$E_{JT}/\hbar\omega$
$[FeCl_4]^{2-}$,[b] Ground State ^5E		
$^5E \otimes \epsilon$	27–82	0.33–1.00
$^5T_2 \otimes \epsilon$	861–1104	10.5–13.5
$^5T_2 \otimes \tau_2(\delta)$	63–59	0.53–0.50
$^5T_2 \otimes \tau_2(\nu)$	202–383	0.71–1.34
$[CoCl_4]^{2-}$,[c] Ground State $^4A_2$		
$^4T_1(F) \otimes \epsilon$	307–367	3.41–4.08
$^4T_1(F) \otimes \tau_2(\delta)$	512–504	4.65–4.58
$^4T_1(F) \otimes \tau_2(\nu)$	163–169	0.57–0.58
$^4T_2 \otimes \epsilon$	652	7.24
$^4T_2 \otimes \tau_2(\delta)$	18–12	0.16–0.11
$^4T_2 \otimes \tau_2(\nu)$	71–91	0.24–0.31
$^4T_1(P) \otimes \epsilon$	528–825	5.87–9.17
$^4T_1(P) \otimes \tau_2(\delta)$	96–150	0.87–1.36
$^4T_1(P) \otimes \tau_2(\nu)$	155–243	0.53–0.84
$[NiCl_4]^{2-}$,[d] Ground State $^3T_1(F)$		
$^3T_1(F) \otimes \epsilon$	436–522	4.95–5.93
$^3T_1(F) \otimes \tau_2(\delta)$	729–717	7.29–7.17
$^3T_1(F) \otimes \tau_2(\nu)$	232–240	0.82–0.84
$^3T_2 \otimes \epsilon$	928	10.6
$^0T_2 \otimes \tau_2(\delta)$	26–16	0.26–0.16
$^3T_2 \otimes \tau_2(\nu)$	101–129	0.36–0.45
$^3T_1(P) \otimes \epsilon$	751–1174	8.53–13.3
$^3T_1(P) \otimes \tau_2(\delta)$	137–213	1.37–2.13
$^3T_1(P) \otimes \tau_2(\nu)$	221–345	0.78–1.22
$[CuCl_4]^{2-}$,[e] Ground State $^2T_2$		
$^2T_2 \otimes \epsilon$	2662–3476	25.6–33.4
$^2T_2 \otimes \tau_2(\delta)$	200–129	1.48–0.95
$^2T_2 \otimes \tau_2(\nu)$	1273–1662	5.05–6.60
$^2E \otimes \epsilon$	83–254	0.79–2.44

[a] Values are listed for the range $e_\pi/e_\sigma = {}^1/_6-{}^1/_4$; the parameters used are from ref 16–20 and from: Smith, D. W. *Struct. Bonding (Berlin)* **1978**, *35*, 87. Basile, L. J.; Ferraro, J. R.; Labonville, P.; Wall, M. C. *Coord. Chem. Rev.* **1973**, *11*, 21. [b] $\Delta_{tet} = -3300$ cm^{-1}, $R = 2.30$ Å, $K_\epsilon = 0.07$, $K_{\tau_2}(\delta) = 0.09$, $K_{\tau_2}(\nu) = 0.84$ mdyn/Å; $\hbar\omega$, $\epsilon = 82$, $\tau_2(\delta) = 119$, $\tau_2(\nu) = 286$ cm^{-1}. [c] $\Delta_{tet} = -3200$ cm^{-1}, $R = 2.28$ Å, $K_\epsilon = 0.06$, $K_{\tau_2}(\delta) = 0.11$, $K_{\tau_2}(\nu) = 0.85$ mdyn/Å; $\hbar\omega$, $\epsilon = 90$, $\tau_2(\delta) = 110$, $\tau_2(\nu) = 290$ cm^{-1}. [d] $\Delta_{tet} = -3800$ cm^{-1}, $R = 2.27$ Å, $K_\epsilon = 0.06$, $K_{\tau_2}(\delta) = 0.11$, $K_{\tau_2}(\nu) = 0.85$ mdyn/Å; $\hbar\omega$, $\epsilon = 88$, $\tau_2(\delta) = 100$, $\tau_2(\nu) = 284$ cm^{-1}. [e] $\Delta_{tet} = -5600$ cm^{-1}, $R = 2.22$ Å, $K_\epsilon = 0.07$, $K_{\tau_2}(\delta) = 0.13$, $K_{\tau_2}(\nu) = 0.61$ mdyn/Å; $\hbar\omega$, $\epsilon = 104$, $\tau_2(\delta) = 135$, $\tau_2(\nu) = 252$ cm^{-1}.

of 2975 cm^{-1} for $^2T_2 \otimes \epsilon$ (cf. Table II), reduced to 1200 cm^{-1} by spin–orbit coupling but still yielding a large enough $E_{JT}/\hbar\omega$ to lead to a static distortion.

For the d^8 $[NiCl_4]^{2-}$ anion however the situation is less clear. In T_d symmetry spin–orbit coupling splits the $^3T_1(F)$ ground state, leaving an inactive Γ_1 level lying lowest, but $E_{JT}/\hbar\omega$ is here significantly less than for $[CuCl_4]^{2-}$, and the still substantial spin–orbit coupling should stabilize the system against any appreciable distortion. Similarly, E_{JT} for the ^5E ground state of d^6 $[FeCl_4]^{2-}$ should be much too small to stabilize any distortion since the E $\otimes$ ϵ coupling involves only e_π contributions, while for d^7 $[CoCl_4]^{2-}$ the ground state is the essentially inactive $^4A_2$ orbital singlet.

Nevertheless, Jahn–Teller-related phenomena due to the Ham effect should in principle be observable for many of the states listed in Tables I and II, but despite extensive spectroscopic studies of the $[CoCl_4]^{2-}$ and $[NiCl_4]^{2-}$ anions[16-20] only cursory attention has as yet been given to this possibility. However, Gerloch and his co-workers have shown[21-23] that for a range of tetrahedral and

(15) Bacci, M. *J. Phys. Chem. Solids* **1980**, *41*, 1267.
(16) Koester, V. J.; Dunn, T. M. *Inorg. Chem.* **1975**, *14*, 1811.
(17) Couch, T. W.; Smith, G. P. *J. Chem. Phys.* **1970**, *53*, 1336.
(18) Mooney, A.; Nuttall, R. H.; Smith, W. E. *J. Chem. Soc., Dalton Trans.* **1973**, *287*, 1920.
(19) Van Stapele, R. P.; Belgers, H. G.; Bongers, P. F.; Zijlstra, H. *J. Chem. Phys.* **1966**, *44*, 3719.
(20) Jesson, J. P. *J. Chem. Phys.* **1968**, *48*, 161.
(21) Gerloch, M.; Slade, R. P. *J. Chem. Soc. A* **1969**, *1012*, 1023.

pseudotetrahedral halo complexes of Co^{II} and Ni^{II} much greater reductions of the spin–orbit coupling constant, below the free-ion value, were observed for the latter than for the former, in studies of the anisotropic magnetic susceptibilities. Since the magnetic behavior is dominated by the nature of the ground state, which for d^7 Co^{II} is the inactive $^4A_2$ state but for d^8 Ni^{II} is the potentially active (T $\otimes$ τ_2 + ϵ) $^3T_1$(F) state, the results were interpreted to support the operation of a significant Ham effect in the Ni^{II} species, partially quenching the spin–orbit coupling. However, apart from [CuCl$_4$]$^{2-}$, the largest calculated E_{JT} values of Table II are generally comparable with the spin–orbit coupling constant (ξ being 410, 533, and 649 cm^{-1} for Fe^{II}, Co^{II}, and Ni^{II}, respectively[9]) so that any calculations of the Ham reduction factors could not use simple perturbation techniques and full diagonalization

in the spin–orbit basis of the appropriate weak-field-state vibronic manifolds would be necessary.

There do however exist extensive data for M^{2+} 3d ions doped into tetrahedral sites in hosts such as CdS, and for these systems Sturge[24] concluded that in most cases T $\otimes$ ϵ coupling would predominate. However, for the $^4T_1$(F) state of Co^{2+}/CdS a substantial Ham effect is observed, reflected in an anomalously small spin–orbit splitting, which was analyzed by Sturge[24] in terms of a mainly T$_1$ $\otimes$ τ_2 coupling, with some T$_1$ $\otimes$ ϵ contribution. This accords strikingly with the present predictions, and it would thus appear eminently worthwhile for further studies to be made of 3d [MCl$_4$]$^{2-}$ species and of other T_d systems, especially for the $^3T_1$(F) and $^4T_1$(F) states of Ni^{II} and Co^{II}, with a view toward identifying any further situations in which T $\otimes$ τ_2 coupling might be dominant.

(22) Gerloch, M.; Manning, M. R. *Inorg. Chem.* **1981**, *20*, 1051.
(23) Gerloch, M.; Hanton, L. R. *Inorg. Chem.* **1981**, *20*, 1046.

(24) Sturge, M. D. *Solid State Phys.* **1967**, *20*, 92.

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Chemistry of [Fe$_6$S$_6$]$^{3+}$ Prismatic Cages. Synthesis, Structural Characterization, and Electronic Structures of the [Et$_4$N]$_3$[Fe$_6$S$_6$L$_6$] Clusters (L = p-CH$_3$C$_6$H$_4$O$^-$, Br$^-$)

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The syntheses of the [Cat]$_3$[Fe$_6$S$_6$L$_6$] clusters (L = Br$^-$, cat = [Et$_3$MeN]$^+$; L = ArS$^-$, Cat = [Et$_4$N]$^+$) are reported. The crystal and molecular structures of [Et$_4$N]$_3$[Fe$_6$S$_6$(p-CH$_3$C$_6$H$_4$O)$_6$] (I) and of [Et$_4$N]$_3$[Fe$_6$S$_6$Br$_6$]·CH$_3$CN (II) are described in detail. I and II crystallize in the monoclinic space groups $P2_1/a$ and $P2_1/n$, respectively, with two molecules in the unit cell. The cell dimensions in I are a = 13.173 (5) Å, b = 19.848 (10) Å, c = 14.304 (4) Å, and β = 98.05 (3)°. In II, a = 14.531 (3) Å, b = 11.028 (2) Å, c = 17.566 (3) Å, and β = 100.69 (1)°. Intensity data for both I and II were collected with a four-circle computer-controlled diffractometer with use of the θ–2θ scan technique. Both structures were solved by conventional methods from 3461 and 2516 reflections for I and II, respectively. The structures were refined by full-matrix least-squares techniques (283 parameters for I and 213 parameters for II) to final R values of 0.075 and 0.049, respectively, for I and II. The anions in I and II contain the [Fe$_6$S$_6$]$^{3+}$ hexagonal-prismatic core, which consists of alternating tetrahedral Fe and triply bridging S atoms. Three of the Fe coordination sites are occupied by core sulfide atoms while the fourth coordination site is filled by the terminal RO$^-$ and Br$^-$ ligands. There are two sets of Fe···Fe distances in the Fe$_6$S$_6$ cores with mean values of 2.761 (5), 2.749 (4) Å and 3.80 (4), 3.81 (2) Å, respectively, for I and II. Similarly, two sets of Fe–S–Fe angles are found for I and II at 74.6 (2) and 74.3 (1)° and 113.8 (2) and 114.2 (9)°. The $\overline{\text{Fe–S}}$ bonds in I and II are 2.276 (5) and 2.274 (4) Å. The $\overline{\text{Fe–O}}$ bond in I is 1.880 (11) Å, and the $\overline{\text{Fe–Br}}$ bond in II is 2.366 (9) Å. The reactivity, cyclic voltammetry, and isotropically shifted NMR spectra of I and II are discussed in detail.

Introduction

The importance of Fe/S centers in the function of the non-heme iron–sulfur proteins (ferredoxins)[1] has generated great interest in Fe/S coordination chemistry. As a result of extensive synthetic, structural, and spectroscopic studies, nearly exact analogues for the 1Fe, 2Fe, and 4Fe centers in the Fe/S proteins are presently available.[2] These synthetic analogues have contributed substantially to our understanding of the biologically occurring Fe/S centers and include the following compounds: [Fe(SR)$_4$]$^{n-}$ (n = 1, 2, (SR)$_2$ = S$_2$-o-xyl;[3] n = 2, R = Ph;[4] n = 1, 2, R = Et, Ph[5]);

[Fe$_2$S$_2$L$_4$]$^{2-}$ (L = EtS$^-$, p-MeC$_6$H$_4$S$^-$;[6a] L = Cl$^-$, Br$^-$, I$^-$;[6b,c] L$_2$ = S$_5$$^{2-}$;[7] L = p-MeC$_6H_4O^-$, C$_4H_4N^-$; L$_2$ = o,o'-C$_{12}$H$_8$O$_2$$^{2-}$[8]); [Fe$_4S_4L_4$]$^{n-}$ (L = aryl, alkanethiolates, n = 2, 3;[2c] L = Cl$^-$, Br$^-$, I$^-$, n = 2;[6b,c] L = 2,4,6-i-Pr-C$_6$H$_2$S$^-$, n = 1;[9] L = PhO$^-$, p-

(1) (a) Orme-Johnson, W. H. *Annu. Rev. Biochem.* **1973**, *42*, 159. (b) Lovenberg, W., Ed. *Iron-Sulfur Proteins*; Academic: New York, 1977; Vol. III. (c) Averill, B. A.; Orme-Johnson, W. H. In *Metal Ions in Biological Systems*; Sigel, H., Ed.; Marcel Dekker: New York, 1978; Vol. VII. (d) Jensen, L. H. In *Iron-Sulfur Proteins*; Lovenberg, W., Ed.; Academic: New York, 1973; Vol. II, Chapter 4. (e) Adman, A. T.; Sieker, L. C.; Jensen, L. H. *J. Biol. Chem.* **1973**, *248*, 2987.
(2) (a) Holm, R. H.; Ibers, J. A. In *Iron-Sulfur Proteins*; Lovenberg, W., Ed.; Academic: New York, 1977; Vol. III, Chapter 7. (b) Holm, R. H. *Acc. Chem. Res.* **1977**, *10*, 427. (c) Berg, J. M.; Holm, R. H. In *Iron-Sulfur Proteins*; Spiro, T., Ed.; Wiley Interscience: New York, 1983; Vol. IV, p 27.

(3) (a) Lane, R. W.; Ibers, J. A.; Frankel, R. B.; Holm, R. H. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 2868. (b) Lane, R. W.; Ibers, J. A. Frankel, R. B.; Papaefthymiou, G. C.; Holm, R. H. *J. Am. Chem. Soc.* **1977**, *99*, 84.
(4) Coucouvanis, D.; Swenson, D.; Baenziger, N. C.; Murphy, C.; Holah, D. G.; Sfarnas, N.; Simopoulos, A.; Kostikas, A. *J. Am. Chem. Soc.* **1981**, *103*, 3350.
(5) (a) Millar, M.; Lee, J.; Koch, S. A.; Fikar, R. *Inorg. Chem.* **1982**, *21*, 4105. (b) Koch, S. A.; Millar, M. *J. Am. Chem. Soc.* **1982**, *104*, 5255. (c) Koch, S. A.; Maelia, L. E.; Millar, M. *J. Am. Chem. Soc.* **1983**, *105*, 5944.
(6) (a) Mayerle, J. J.; Denmark, S. E.; De Pamphilis, B. V.; Ibers, J. A.; Holm, R. H. *J. Am. Chem. Soc.* **1975**, *97*, 1032. (b) Wong, G. B.; Bobrik, M. A.; Holm, R. H. *Inorg. Chem.* **1978**, *17*, 578. (c) Bobrik, M. A.; Hodgson, K. O.; Holm, R. H. *Inorg. Chem.* **1977**, *16*, 1851.
(7) Coucouvanis, D.; Swenson, D.; Stremple, P.; Baenziger, N. C. *J. Am. Chem. Soc.* **1979**, *101*, 3392.
(8) Coucouvanis, D.; Salifoglou, A.; Kanatzidis, M. G.; Simopoulos, A.; Papaefthymiou, V. *J. Am. Chem. Soc.* **1984**, *106*, 6081.
(9) O'Sullivan, T.; Millar, M. M. *J. Am. Chem. Soc.* **1985**, *107*, 4096.