Binuclear Metal Complexes. 58.[1] Synthesis and Properties of Mixed-Valence Diiron(III,IV) Complexes of Salen Analogs with Pendant Thioether Group

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Iron complexes of the composition $[Fe_2(L)_2O]PF_6$ have been obtained with *N,N'*-disalicylidene-2-methyl-4-(1-methylethylthio)-1,2-butanediamine (H_2L^1) and *N,N'*-disalicylidene-2-methyl-4-ethylthio-1,2-butanediamine (H_2L^2). They were characterized as mixed-valence diiron(III,IV) complexes composed of high-spin iron(III) and low-spin iron(IV). Cryomagnetic measurements demonstrated the operation of an antiferromangetic spin-exchange interaction (J=−12.3—−13.9 cm^{-1}) between the Fe^{III} and Fe^{IV} ions. ESR signals at liquid nitrogen temperature (g=4.03 and 2.00) were reasonably attributed to the ground spin state (S_T=3/2) in the spin-coupled dimer. In the Mössbauer spectra two quadrupole splitting doublets due to iron(III) and iron(IV) were observed. The complexes were discussed in comparison with mixed-valence complexes of *N,N'*-disalicylideneethylenediamine (H_2salen), $[Fe_2(salen)_2O]X$, composed of high-spin iron(III) and high-spin iron(IV).

It is worthwhile to design pentadentate ligands consisting of a planar unsaturated tetradentate system and an axial base, because such a pentacoordinate environment is often seen at the active site of metalloenzymes such as hemoglobin[2] and myoglobin.[3] For this purpose there have been synthesized some pentadentate salen analogs (H_2salen=*N,N'*-disalicylideneethylenediamine) possessing a pyridyl,[4] hydroxyphenyl,[5] methoxyphenyl,[5] or alkylthio group[6,7] as the pendant group. Salen analogs with thioether pendant group were recently synthesized in our laboratory.[6] These ligands formed pentacoordinate cobalt(II) complexes with the thioether sulfur at the axial site under nitrogen atmosphere while hexacoordinate O_2-adducts in the presence of molecular oxygen. In this study we have synthesized iron complexes of salen analogs, *N,N'*-disalicylidene-2-methyl-4-(1-methylethylthio)-1,2-butanediamine (H_2L^1) and *N,N'*-disalicylidene-2-methyl-4-ethylthio-1,2-butanediamine (H_2L^2) (see Fig. 1). The objects of this study are to characterize the complexes and to elucidate the sulfur coordination effect on the property of the complexes. A similar ligand, (*S*)-*N,N'*-disalicylidene-4-methylthio-1,2-butanediamine, was prepared by Amundsen et al.[7] However, they found no evidence of thioether coordination in its iron(III) complex.

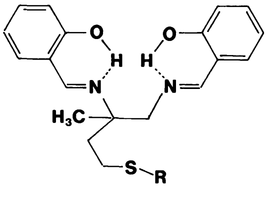
Fig. 1. Chemical structure of ligands: R = i-C_3H_7, H_2L^1; R = C_2H_5, H_2L^2.

Experimental

Preparation. The synthesis of H_2L^1 is described in the previous paper.[6] H_2L^2 was prepared in this study in nearly the same way as that of H_2L^1 except for the use of 4-ethylthio-2-butanone instead of 4-(1-methylethylthio)-2-butanone as the starting material.

Iron complexes were obtained as follows. Iron(II) sulfate heptahydrate (1×10^{-3} mole) and the ligand (1×10^{-3} mole) were dissolved in ethanol (50 cm^3), and the mixture was heated at 80 °C for 30 min. To this was added NH_4PF_6 (2×10^{-3} mole), and the mixture was heated for 3 h with stirring. Insoluble materials were separated by filtration, and the solvent was evaporated to dryness. The residue was dissolved in dichloromethane, and the solution was allowed to stand for one week. The crude product thus obtained was dissolved in dichloromethane and reprecipitated by adding ether to this solution. This operation was repeated five times to give brown microcrystals.

$[Fe_2(L^1)_2O]PF_6$, yield ca. 90 mg. Found: C, 50.81; H, 5.04; N, 5.40%. Calcd for $C_{44}F_6Fe_2H_{52}N_4O_5PS_2$; C, 50.92; H, 5.05; N, 5.40%.

$[Fe_2(L^2)_2O]PF_6$, yield ca. 70 mg. Found: C, 49.98; H, 4.91; N, 5.66%. Calcd for $C_{42}F_6Fe_2H_{48}N_4O_5PS_2$: C, 49.96; H, 4.79; N, 5.55%.

Physical Measurements. Infrared spectra were obtained on a Hitachi-Parkin-Elmer 225 grating IR spectrometer on KBr disks. Electronic spectra were recorded on a Shimadzu MPS-5000 spectrometer. Magnetic susceptibilities were measured by the Faraday method in the range 80—300 K. The apparatus was calibrated using $Hg[Co(NCS)_4]$.[8] Diamagnetic corrections were carried out using Pascal's constants.[9] Cyclic voltammograms and differential pulse polarograms were recorded on a Yanagimoto P-1000 voltammetric analyzer in freshly distilled dichloromethane. The measurements were carried out with a three-electrode

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cell equipped with a glassy-carbon working electrode, a platinum-coil auxiliary electrode, and a calomel electrode as the reference electrode. Tetrabutylammonium perchlorate (0.1 mol dm^{-3}) was added as the supporting electrolyte. All the potentials were normalized by the use of ferrocene as an internal standard.[10] ESR spectra (X-band) were recorded on a JEOL JES-FE-3X instrument on powder samples at room temperature and liquid nitrogen temperature. Mössbauer spectra were measured with a constant-acceleration spectrometer (Ausin Science Associates) using a cobalt 57 source diffused into palladium foil. All the spectra were fitted to the Lorentzian line shape using the least-squares method. The velocity scale was normalized with respect to the center of the spectrum of metallic iron at 297 K.

Results and Discussion

Analytical results satisfactorily coincided with the formula $[Fe_2(L)_2O]PF_6$, which suggested the formation of oxo-bridged mixed-valence diiron(III,IV) complexes.

The effective magnetic moments (μ_{eff} per metal ion) for the L^1- and L^2-complexes were 4.28 and 4.36 BM, respectively. As the temperature was lowered to the liquid nitrogen temperature, the moments decreased to 3.45 and 3.58 BM, respectively. The temperature-dependence of the magnetic moments is presumably due to an antiferromagnetic spin-exchange interaction through the oxo-bridge but not due to other effects such as spin-crossover phenomenon.

For analyzing the magnetism of the complexes, a spin Hamiltonian for an isotropic exchange interaction for a dimer ($\mathcal{H}=-2J\hat{S}_1\cdot\hat{S}_2$) was adopted, where J is the exchange integral and $\hat{S}_1$ and $\hat{S}_2$ are the spin operators for metals 1 and 2, respectively. Magnetic susceptibility equation for the case $Fe^{III}(S=5/2)$-$Fe^{IV}(S=2)$ have been derived by Wojciechowski as follows:[11]

$$\chi_M = \frac{Ng^2\beta^2}{4kT} \times \frac{\begin{array}{c}165\exp(-24J/kT)+84\exp(-15J/kT)\\ +35\exp(-8J/kT)+10\exp(-3J/kT)+1\end{array}}{\begin{array}{c}5\exp(-24J/kT)+4\exp(-15J/kT)\\ +3\exp(-8J/kT)+2\exp(-3J/kT)+1\end{array}} + N\alpha$$

With this equation Wollmann and Hendrickson well explained the magnetisms of their mixed-valence diiron(III,IV) complexes, $[Fe_2(salen)_2O]X$, which is structurally similar to the present complexes. When this equation was applied to the present complexes, however, very poor fits to the experimental data were obtained.

It is noted that the magnetic moments for the L^1- and L^2-complexes are considerably lower than that of $[Fe_2(salen)_2O]PF_6$ at room temperature (≈4.7 BM at 300 K), but are higher than that of $[Fe_2(salen)_2O]PF_6$ at liquid nitrogen temperature (≈3.0 BM at 78 K). This suggests that for the present complexes the highest total-spin quantum number is smaller than that ($S_T=9/2$) for $Fe^{III}(S=5/2)$-$Fe^{IV}(S=2)$ and the lowest total-spin quantum number is larger than that ($S_T=1/2$) for $Fe^{III}(S=5/2)$-$Fe^{IV}(S=2)$. Such a situation occurs only when either of the iron(III) or iron(IV) is in low-spin state. Therefore, magnetic simulations were attempted with the susceptibility equations for $Fe^{III}(S=5/2)$-$Fe^{IV}(S=1)$ and $Fe^{III}(S=1/2)$-$Fe^{IV}(S=2)$, together with those for $Fe^{III}(S=3/2)$-$Fe^{IV}(S=2)$, Fe^{III}-$(S=3/2)$-$Fe^{IV}(S=1)$, $Fe^{III}(S=1/2)$-$Fe^{IV}(S=2)$, and Fe^{III}-$(S=1/2)$-$Fe^{IV}(S=1)$. As the result, only the equation for the $Fe^{III}(S=5/2)$-$Fe^{IV}(S=1)$ case,

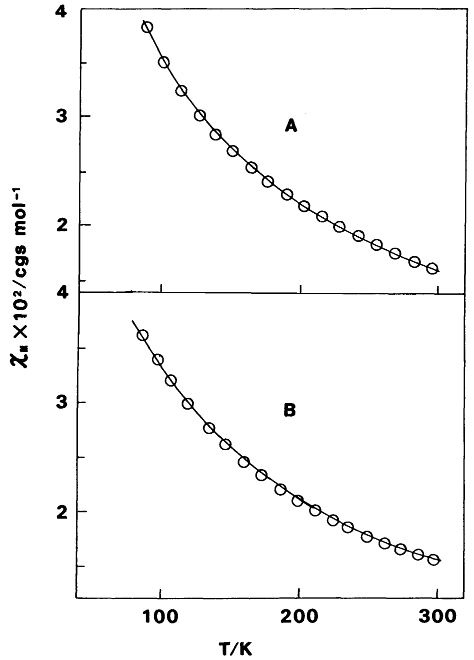

Fig. 2. Temperature-variations of magnetic susceptibility of $[Fe_2(L^1)_2O]PF_6$ (A) and $[Fe_2(L^2)_2O]PF_6$ (B). Solid curves are drawn based on the equation for the spin-coupled (S=5/2)-(S=1) system (see text), with the paramenters $J=-12.3$ cm^{-1} and $g=2.01$ for A and $J=-13.9$ cm^{-1} and $g=2.00$ for B.

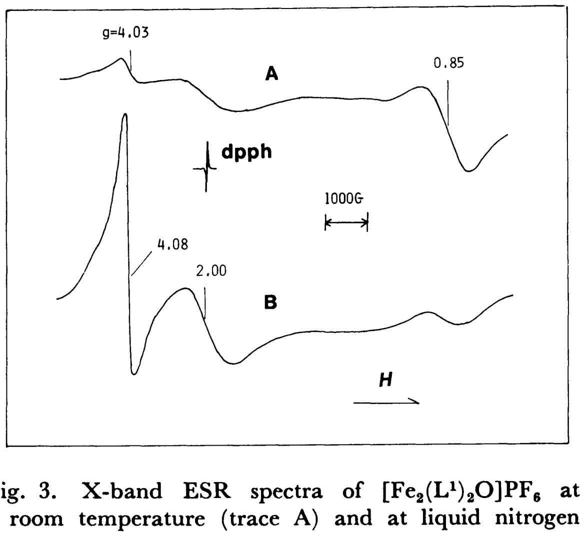

Fig. 3. X-band ESR spectra of $[Fe_2(L^1)_2O]PF_6$ at room temperature (trace A) and at liquid nitrogen temperature (trace B).

$$\chi_M = \frac{Ng^2\beta^2}{4kT} \times \frac{84\exp(-12J/kT)+35\exp(-5J/kT)+10}{4\exp(-12J/kT)+3\exp(-5J/kT)+2} + N\alpha,$$

could reasonably explain the temperature variation of magnetic susceptibilities for the L^1- and L^2-complexes as shown in Fig. 2. The magnetic parameters obtained by best-fit technique are $J=-12.3\ cm^{-1}$ and $g=2.01$ for the L^1-complex and $J=-13.9\ cm^{-1}$ and $g=2.00$ for the L^2-complex; the temperature-independent paramagnetism $N\alpha$ being assumed to be zero in this simulation.

Thus, magnetic investigations demonstrate the presence of low-spin iron(IV) in the present complexes. It must be emphasized that the complexes $[Fe_2(salen)_2O]X$ involve high-spin iron(IV).[12] The low-spin state of the iron(IV) in $[Fe_2(L)_2O]PF_6$ presumably results from the coordination of the pendant thioether sulfur to the metal ion. On the other hand, it is unclear at present whether the sulfur coordination to the iron(III) occurs or not in these complexes.

X-band ESR spectra of the L^1-complex were obtained on powder sample at room temperature and liquid nitrogen temperature (Fig. 3). The spectrum at room temperature (trace A) exhibits three signals at g=4.03, 2.00, and 0.85. At liquid nitrogen temperature (trace B) the g=0.85 signal practically disappeared, whereas the $g\approx4.0$ and 2.0 signals increased their intensities. It is likely that the g=4.08 and 2.00 signals in trace B are due to the ground spin state and the g=0.85 signal in trace A is due to one of the excited spin states of the mixed-valence diiron(III,IV) complex. The low temperature spectrum (trace B) can be reasonably interpreted in terms of the total-spin ground state ($S_T=3/2$) of the spin-coupled $Fe^{III}(S=5/2)$-$Fe^{IV}(S=1)$ dmer; the g=2.00 and 4.08 signals being attributed to the $g_{/\!/}$ and $g_{\perp}$ components of the $(+1/2\leftrightarrow-1/2)$ transition, respectively. The signal due to the $(+3/2\leftrightarrow+1/2)$ and $(-1/2\leftrightarrow-3/2)$ transitions are not observed probably because of a large zero-field splitting owing to the low molecular symmetry and the spin-orbit coupling interaction. Therefore, the ESR spectral result also strongly supports the presence of low-spin iron(IV) in $[Fe_2(L)_2O]PF_6$. In contrast to this, for $[Fe_2(salen)_2O]X$ only a broad signal with a line width of ≈650 G has been observed near g=2.0.[12]

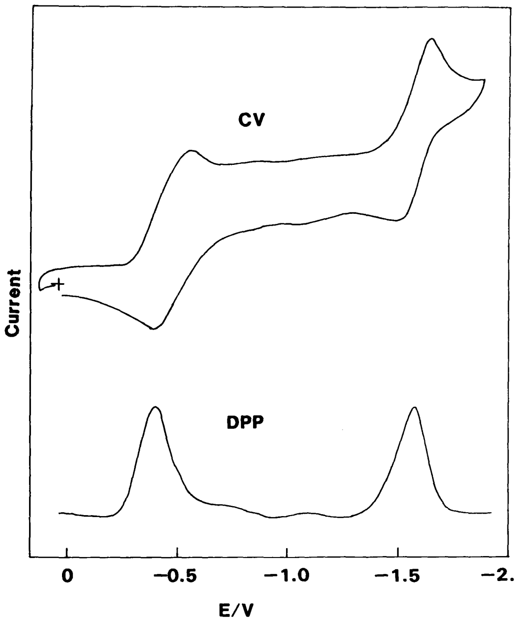

Fig. 4. Cyclic voltammogram and differential pulse polarogram of $[Fe_2(L^1)_2)]PF_6$: concd=1.02×10^{-3} M (1 mol dm^{-3}); scan rate=0.01 V s^{-1} for both CV and DPP; in CH_2Cl_2.

Cyclic voltammogram (CV) and differential pulse polarogram (DPP) for the L^1-complex are shown in Fig. 4. The CV and DPP both showed two reduction waves at −0.40 and −1.58 V. The L^2-complex also showed two reduction waves at −0.56 and −1.52 V. For analyzing the electrochemical behaviors of the present complexes, the electrochemical data for $[Fe(salen)]_2O$[13] seemed helpful. In our measurements, this complex showed one reduction wave at −1.55 V, attributable to the process $Fe^{III}Fe^{III}/Fe^{II}Fe^{III}$.[13] Notably this potential well corresponds to the second reduction potential for $[Fe_2(L)_2O]PF_6$. Thus, we may assign the second wave to the $Fe^{III}Fe^{III}/Fe^{II}Fe^{III}$ process and the first wave to the $Fe^{III}Fe^{IV}/Fe^{III}Fe^{III}$ process. Electrochemical results, therefore, support the fact that $[Fe_2(L)_2O]PF_6$ are mixed-valence diiron(III,IV) complexes.

The ^{57}Fe Mössbauer spectra of the L^1-complex were obtained at 296, 80, and 15 K. The spectra were practically independent of temperature. The spectrum at 80 K is shown in Fig. 5. The spectrum consists of two doublets of closely similar isomer shifts and quadrupole splittings, implying the presence of two kinds of iron, i.e., Fe^{III} and Fe^{IV}. The spectrum was analyzed by computer technique into four peaks with nearly equal intensity and half-band width (Fig. 5). We tentatively assigned the peaks 1 and 3 to the iron(IV) and the peaks 2 and 4 to the iron(III). Another pairing (1 and 4; 2 and 3) is also possible, but our assignment is based on the general concept that

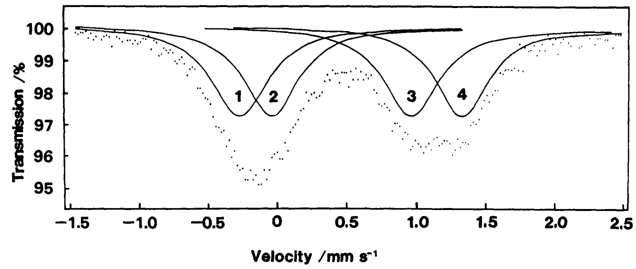

Fig. 5. Mössbauer spectrum of $[Fe_2(L^1)_2O]PF_6$ at 80K.

Table 1. Mössbauer Parameters for $[Fe_2(L^1)_2O]PF_6$

T/K	Fe^{III}		Fe^{IV}	
	δ	Δ	δ	Δ
295	0.463	1.478	0.310	1.054
80	0.647	1.399	0.343	1.256
15	0.673	1.368	0.344	1.296

δ, isomer shift/mm s^{-1}; Δ, quadrupole splitting/mm s^{-1}.

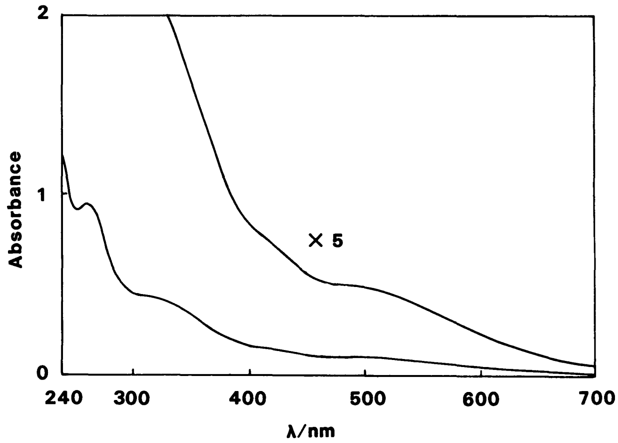

Fig. 6. Electronic spectra of $[Fe_2(L^1)_2O]PF_6$: concd= 2.377×10^{-5} M; in CH_2Cl_2.

the isomer shift for iron(IV) is smaller than that for iron(III). The results are given in Table 1. The isomer shift and quadrupole splitting assigned to the high-spin iron(III) are quite reasonable. On the other hand, Mössbauer spectral data for low-spin iron(IV) are very limited.14—16) Of these complexes, tris(disubstituted dithiocarbamato)iron(IV) tetrafluoroborates show isomer shift falling in the range 0.45—0.57 mm s^{-1} relative to sodium pentacyanonitrosylferrate(III).16) Thus the isomer shift assigned to the iron(IV) of the L^1-complex does not seem unreasonable.

From the above results, it is concluded that the $[Fe_2(L)_2O]PF_6$ complexes are mixed-valence diiron(III,IV) complexes, probably bridged by oxo group. Oxo-bridged diiron(III,III) complexes have been characterized by an intense IR band in the 800—900 cm^{-1} region, which is assigned to the asymmetric Fe–O–Fe stretching mode.17) The present complexes do not show such a band in the 800—900 cm^{-1} region. We also examined far IR spectra of the complexes, in comparison with the spectra of the nickel(II) complexes of H_2L^1 and H_2L^2. However, any characteristic IR band was seen for the diiron complexes. It should be noted that $[Fe_2(salen)_2O]X$12) also showed no IR band attributable to the Fe–O–Fe stretch. As suggested by Wollmann and Hendrickson,12) it is probable that the Fe–O–Fe band of $[Fe_2(L)_2O]PF_6$ is weakened in intensity, shifted in position, and obscured by ligand vibrations.

Mixed-valence complexes generally show intervalence transfer bands in visible or near IR region.18—20) The electronic spectra of $[Fe_2(L)_2O]PF_6$ in dichloromethane showed absorption bands at 260, 320, 420, and 500 nm. The spectrum of the L^1-complex is given in Fig. 6. No absorption was found in the near IR region. Despite the different spin state of iron(IV), $[Fe_2(L)_2O]PF_6$ showed an absorption spectrum very similar to that of $[Fe_2(salen)_2O]PF_6$.12) By the inspection of the spectra of $[Fe(salen)]_2O$ and $[Fe_2(salen)_2O]X$, Wollmann and Hendrickson tentatively assigned the ≈500 nm band of the latter complex to the intervalence transfer band.12) According to Hush,20) the energy of an intervalence transfer band should vary with $(1/n^2)$-$(1/D)$ of solvent, where n is the refractive index and D the dielectric constant of solvent. The electronic spectra of $[Fe_2(L)_2O]PF_6$ were measured in various solvents (CH_2Cl_2, $CHCl_3$, CH_3CN, CH_3OH, dioxane), and it was found that the frequency of the ≈500 nm band was practically independent of the solvents. Probably this band is not intervalence transfer band but a charge transfer band from the phenolic oxygen to the iron(III) or iron(IV). Since intramolecular electron transfer from high-spin iron(III) to low-spin iron(IV) should produce the mixed-valence state composed of intermediate-spin iron(III) and high-spin iron(IV), the intervalence transfer band for $[Fe_2(L)_2O]PF_6$ must be located at a higher energy region than 500 nm and concealed by more intense absorptions.

References

1) Part 57: M. Handa, Z. J. Zhong, M. Mikuriya, H. Ōkawa, and S. Kida, *J. Chem. Soc., Dalton Trans,* in press.

2) S. E. V. Phillips, *Nature (London),* **273**, 247 (1978).

3) B. Shaanan, *Nature (London),* **296**, 683 (1982).

4) J. P. Collman, H. Takaya, B. Winkler, L. Libit, S. S. Koon, G. A. Rodley, and W. T. Robinson, *J. Am. Chem. Soc.,* **95**, 1656 (1973).

5) W. Kanda, H. Ōkawa, and S. Kida, *Bull. Chem. Soc. Jpn.,* **56**, 3268 (1983).

6) K. Nakamoto, H. Oshio, H. Ōkawa, W. Kanda, K. Horiuchi, and S. Kida, *Inorg. Chim. Acta,* **108**, 231 (1985).

7) A. R. Amundsen, J. Whelan, and B. Bosnich, *Inorg. Chem.,* **18**, 206 (1979).

8) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.,* **1959**, 331.

9) F. E. Mabbs and D. J. Machin, "Magnetism and Transition Metal Complexes," Chapman and Hall, London (1973), p. 5.

10) R. R. Gagne, C. A. Koval, and G. C. Lisensky, *Inorg. Chem.,* **19**, 2854 (1980).

11) W. Wojciechowski, *Inorg. Chem. Acta,* **1**, 324 (1967).

12) R. G. Wollmann and D. N. Hendrickson, *Inorg. Chem.,* **16**, 723 (1977).

13) S. E. Wenk and F. A. Schultz, *J. Electroanal. Chem.,* **101**, 89 (1979).

14) G. Simonneaux, W. F. Scholz, C. A. Reed, and G.

Lang, *Biochim. Biophys. Acta,* **716**, 1 (1982).

15) J. T. Groves, R. Quinn, T. J. McMurry, M. Nakamura, G. Lang, and B. Boso, *J. Am. Chem. Soc.,* **107**, 354 (1985).

16) E. A. Pasek and D. K. Straub, *Inorg. Chem.,* **11**, 259 (1972).

17) K. S. Murray, *Coord. Chem. Rev.,* **12**, 1 (1974).

18) M. B. Robin and P. Day, *Adv Inorg. Chem. Radiochem.,* **10**, 247 (1967).

19) G. C. Allen and N. S. Hush, *Prog. Inorg. Chem.,* **8**, 357 (1967).

20) N. S. Hush, *Prog. Inorg. Chem.,* **8**, 391 (1967).