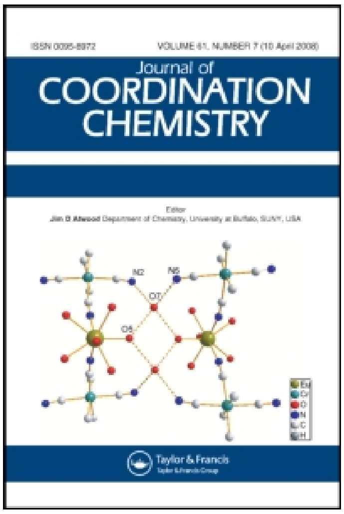

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Olavi Siiman[a]; Mark Wrighton[a]; Harry B. Gray[a]
[a] Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California

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MOLECULAR AND ELECTRONIC STRUCTURE OF BIS(TETRAPHENYLDITHIOIMIDODIPHOSPHINATO)MANGANESE(II)

OLAVI SIIMAN, MARK WRIGHTON and HARRY B. GRAY[†]

Contribution No. 4477 *from the Arthur Amos Noyes Laboratory of Chemical Physics*
California Institute of Technology, Pasadena, California 91109

Complexes of the type $[SPR_2NPR_2S]_2M$ (M= Fe,Co,Ni, Zn; $R = CH_3, C_6H_5$) have been shown to have a tetrahedral MS_4 core structure.[1–3] Because of its potential utility as a model for biologically important d^5 MS_4-type tetrahedral structures, we have extended the series to include bis(tetraphenyldithioimidodiphosphinato)manganese(II), (I). We report herein the principal geometrical structural details as well as magnetic and spectral measurements which establish the nature of the ground state and the lowest excited electronic states of (I).

When $Na(SP\phi_2NP\phi_2S]$[4] is mixed with Mn(acetate)$_2$ in water and the product is recrystallized from dichloromethane–hexane solutions, pink crystals[5] of (I) are formed. Crystals of (I) belong to the triclinic space group, $P\bar{1}$, with $a = 13.549(4)$, $b = 14.334(4)$, $c = 13.824(3)$ Å, $\alpha = 82.17(2)$; $\beta = 110.50(2)$, $\gamma = 114.11(2)°$, $V = 2295(2)$ Å^3, $\rho_0 = 1.37(2)$ g/cc, and $\rho_c = 1.377$ g/cc for $M = 951.97$, $Z = 2$. Intensity data from 8178 independent reflections ($\sin\theta_{max} = 0.43$ for MoKα radiation) were collected on a full-circle Syntex diffractometer. Patterson, Fourier, and least squares refinement calculations incorporating all non-hydrogen atoms have yielded a residual index, $R = 0.073$.

Figure 1 shows a stereoscopic view of the molecular structure of (I). Bond angles around the approximately tetrahedral Mn atom are: S(2)–Mn–S(1)=111.7(1), S(3)–Mn–S(1)=110.8(1), S(4)–Mn–S(1)=106.4(1), S(3)–Mn–S(2)=107.4(1), S(4)–Mn–S(2)=108.5(1), S(4)–Mn–S(3)=112.1°(1). The Mn–S bond distances vary from 2.427 to 2.455 Å, somewhat greater than Ni–S = 2.282[2] and Fe–S =2.360[3] bond distances in two tetramethyldithioimidodiphosphinates. Average bond distances and angles in the chelate rings of (I) are: Mn–S, 2.443(2); S–P, 2.013(2); P–N, 1.588(4); P–C, 1.810(5) Å; Mn–S–P, 99.9(1); S–P–N, 118.7(2); P–N–P, 133.3(3); S–P–C, 107.9(2); N–P–C, 107.8(2); C–P–C, 106.0(2)°.

The μ_{eff} value of 5.75 B.M. of a solid sample of (I) is consistent with a $^6A_1$ ground electronic state. A 77°K excitation spectrum of (I) establishes the positions of the lowest ligand field bands (Figure 2).[6] The first six of nine possible spin-forbidden sextet — quartet transitions (to ^4G, ^4D, ^4P, and ^4F states) for tetrahedral symmetry are observed between 14,000 and 30,000 cm^{-1}. The band maxima are located near 18,520 (0.32), 20,530 (1.03), 21,280 (0.88), 23,810 (0.76), 25, 640 (1.76), and 28,820

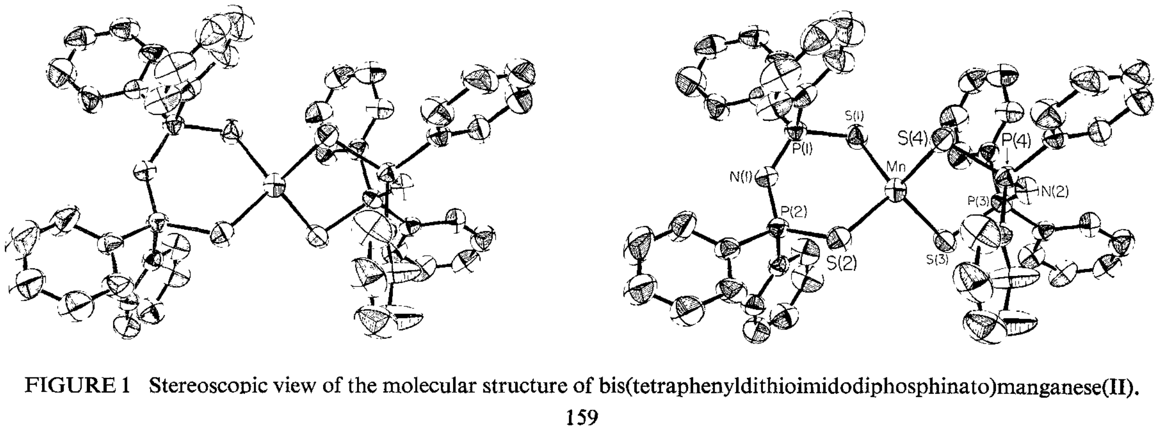

FIGURE 1 Stereoscopic view of the molecular structure of bis(tetraphenyldithioimidodiphosphinato)manganese(II).

(10.23), and are attributed to the $^6A_1$ — $^4T_1$ (^4G), $^4T_2$ (^4G), ($^4A_1$ (^4G), ^4E (^4G)), $^4T_2$ (^4D), ^4E (^4D), and $^4T_1$ (^4P) transitions, respectively.[7] The positions of these transitions correspond closely to the analogous bands in the spectrum of Mn^{2+} doped in ZnS,[8] as marked in Figure 2. Standard Tanabe-Sugano analysis[9] of the ligand field spectrum of (I) yields 10 Dq = 4570 and $B = 653$ cm^{-1} (Dq/B = 0.7; C/B = 4.48).

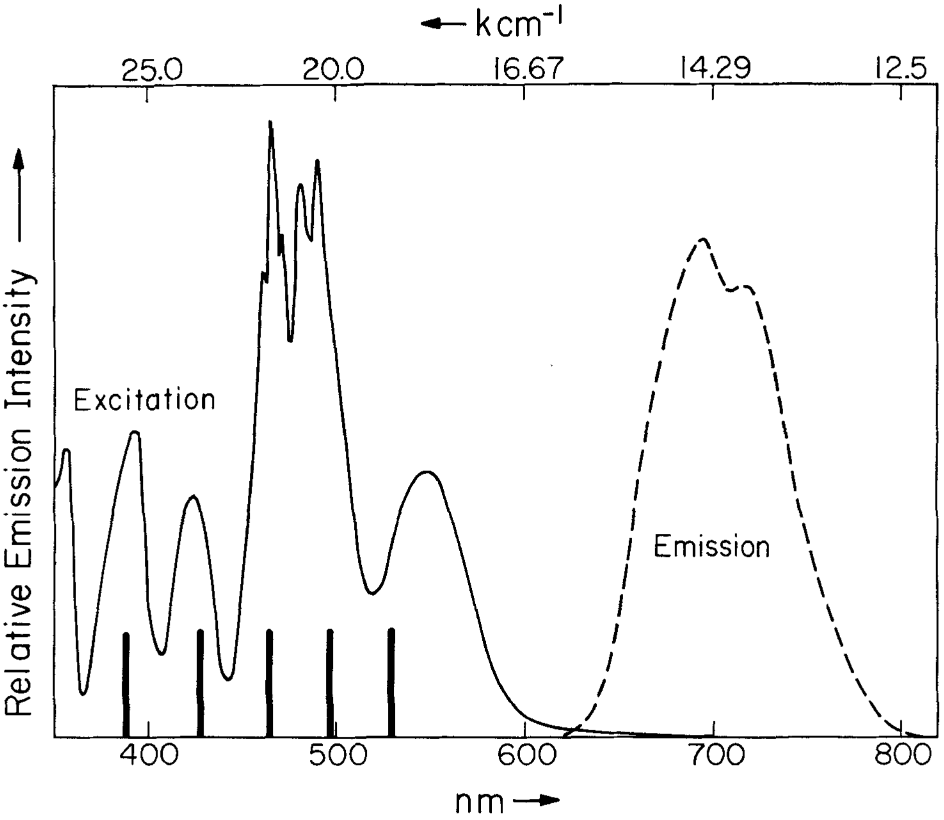

FIGURE 2 Electronic excitation and emission spectra of a solid sample of (I) at 77°K.

Luminescence studies of Mn^{2+} complexes have suggested the generalization that a given type of O_h environment will exhibit lower energy emission than an analogous T_d site.[10] The luminescence of Mn^{2+} in T_d sites of ZnS is narrow (500 cm^{-1} half-width) and shows very little shift of the emission maximum, 17,891 cm^{-1}, when compared to the first absorption maximum at 18,850 cm^{-1}. In marked contrast to the Mn^{2+} (ZnS) data, (I) luminesces with a 1665 cm^{-1} half-width and the emission maximum (14,347 cm^{-1}) is considerably red-shifted from the first absorption maximum at 18,520 cm^{-1}. It is reasonable to assume that the large differences in the emission spectra of Mn^{2+} (ZnS) and (I) are due mainly to the greater rigidity of the sulfur-donor environment in the former case. Thus the possibility is suggested that a detailed comparison of the emission and absorption spectra of biologically important d^5 MS_4-type complexes such as iron(III) rubredoxin[11] could yield valuable information concerning the relative rigidity of the sulfur-donor environment, in addition to providing the usual characterization of the strength of the ligand field.

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6. The optical spectrum of (I) has been measured for the powdered solid, in dichloromethane solution, and for a single crystal; the positions of absorption band maxima agree well with the excitation spectrum.
7. Molar extinction coefficients obtained from a single crystal of 0.047 cm thickness are given in parentheses.
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