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## Absorption Spectra and Electronic Structures of Some Tetrahedral Manganese(II) Complexes

By F. ALBERT COTTON,<sup>1a</sup> DAVID M. L. GOODGAME<sup>1b</sup> AND MARGARET GOODGAME<sup>1c</sup>

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The visible and near ultraviolet absorption spectra of a number of salts of the tetrahalomanganese(II) ions,  $[\text{MnX}_4]^{2-}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ), have been measured in the solid state and in various solvents at  $\sim 25^\circ$ . It also has been observed that several of the compounds exhibit green fluorescence and that two of them are triboluminescent. The sensitivity of the complex anions to solvolysis or other effects in some solvents has been observed and the salutary effect of adding an excess of the  $\text{RX}$  compound corresponding to  $\text{R}_2[\text{MnX}_4]$  has been demonstrated. The spectral data are qualitatively in agreement with predictions of ligand field theory. While quantitative treatment could not be carried out for  $[\text{MnI}_4]^{2-}$ , the data for the chloro and bromo complexes have been treated to obtain values of  $\Delta$ ,  $B$  and  $C$ .

### Introduction

The electronic structures of manganese(II) ( $3d^5$ ) high spin complexes have occasioned much theoretical interest,<sup>2-8</sup> and there has been considerable experimental study of several of the octahedral ones.<sup>4-8</sup> However, despite the presumed existence of some tetrahedral manganese(II) complexes,<sup>5,9-11</sup> and, more recently, the certainty of the existence of others,<sup>12</sup> no systematic study of their spectra has been reported, although fragmentary data may be found.<sup>5,12,13,14</sup> We have prepared salts of the tetrahalo anions,  $[\text{MnCl}_4]^{2-}$ ,  $[\text{MnBr}_4]^{2-}$  and  $[\text{MnI}_4]^{2-}$  and recorded their reflectance spectra and transmission spectra both as mulls in nujol or hexachlorobutadiene and in solution. As will be shown later, quantitative theoretical analysis of the experimental data in terms of simple ligand field theory (*i.e.*, using only the Racah parameters  $B$  and  $C$ , and  $\Delta$ , the modulus of ligand field strength, as adjustable parameters) is not wholly successful, but nevertheless certain valuable conclusions can be obtained from the approximate analysis which has been made.

The results of this work should be of interest in connection with the role of tetrahedrally coordinated manganese(II) in a number of technologically important phosphors such as  $[\text{Zn}(\text{Mn})_2\text{SiO}_4]$ .<sup>15</sup>

### Experimental

**Preparation of Compounds. Pyridinium Tetrachloromanganate(II).**—This complex was prepared by one of the methods described by Taylor.<sup>10</sup> A solution of anhydrous manganous chloride (2.52 g., 0.02 mole) in hot absolute ethanol (16 ml.) was added to a solution of pyridine hydro-

chloride (4.88 g., 0.044 mole) also in absolute ethanol (7 ml.). Pale green needles separated as the solution cooled. These were filtered off, washed with absolute ethanol and dried *in vacuo* over sulfuric acid; yield 68%, m.p.  $152^\circ$  (lit.<sup>10</sup>  $152\text{--}155^\circ$ ).

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_{12}\text{Cl}_4\text{MnN}_2$ : C, 33.64; H, 3.39; N, 7.85. Found: C, 33.73; H, 3.36; N, 7.82.

**Methyltriphenylphosphonium Tetrachloromanganate(II).**—This pale green compound was prepared in the same way as the pyridinium complex; yield 62%, m.p.  $216^\circ$ .

*Anal.* Calcd. for  $\text{C}_{38}\text{H}_{36}\text{Cl}_4\text{MnP}_2$ : C, 60.74; H, 4.83; Cl, 18.87; P, 8.24. Found: C, 60.56; H, 4.75; Cl, 18.63; P, 8.06.

**Tetramethylammonium Tetrachloromanganate(II).**—This was prepared by a method analogous to that used for the pyridinium compound. The complex precipitated as very small crystals immediately on mixing the hot ethanolic solutions of the reactants. It had a very faint yellow color; yield 71%.

*Anal.* Calcd. for  $\text{C}_8\text{H}_{20}\text{Cl}_4\text{MnN}_2$ : C, 27.84; H, 7.01; N, 8.12. Found: C, 27.38; H, 6.65; N, 7.68. The compound did not melt on heating to  $400^\circ$ .

It was very slightly soluble in the lower alcohols on heating but insoluble in other organic solvents.

When the preparation was carried out using hydrated manganous chloride the product was pale pink. Moreover, the analysis was not satisfactory. (Found: C, 26.52; H, 6.59; N, 7.39.) The compound could not be recrystallized. The impurity was not  $[\text{MnCl}_2(\text{H}_2\text{O})]^-$ , reported by Taylor<sup>10</sup> for the complex  $[\text{C}_5\text{H}_5\text{NH}][\text{MnCl}_2(\text{H}_2\text{O})]$ , since the infrared spectrum of the pink compound contained no bands attributable to O-H stretching.

**Tetraethylammonium Tetrabromomanganate(II).**—This was prepared by the method of Jørgensen<sup>4</sup> in 42% yield with m.p.  $300^\circ$ .

*Anal.* Calcd. for  $\text{C}_{16}\text{H}_{40}\text{Br}_4\text{MnN}_2$ : C, 30.26; H, 6.35; N, 4.41. Found: C, 30.80; H, 6.52; N, 4.47.

**Tetra-*n*-butylammonium Tetra-iodomanganate(II).**—A solution of manganous iodide (1.55 g., 0.005 mole) in ethyl acetate (65 ml.) was treated with finely-powdered tetra-*n*-butylammonium iodide (3.69 g., 0.01 mole) and the mixture was heated, forming a pale yellow solution and a yellow oil. Addition of absolute ethanol (6 ml.) to the hot mixture produced a homogeneous yellow solution, which was filtered. On cooling, pale green needles separated, which were filtered off, washed with ethyl acetate and dried *in vacuo*; yield 60%, m.p.  $148^\circ$ .

*Anal.* Calcd. for  $\text{C}_{32}\text{H}_{72}\text{I}_4\text{MnN}_2$ : C, 36.69; H, 6.93; N, 2.67. Found: C, 36.56; H, 6.76; N, 2.84.

**Physical Measurements.**—Electrolytic conductances were measured with a Serfass bridge, using a conventional cell calibrated with aqueous potassium chloride. The values obtained in  $\Omega^{-1} \text{mole}^{-1}$  for approximately  $10^{-3} M$  solutions in nitromethane were the following:  $(\text{PyH})_2[\text{MnCl}_4]$ , 114;  $(\text{Et}_4\text{N})_2[\text{MnBr}_4]$ , 197;  $(\text{Bu}_4\text{N})_2[\text{MnI}_4]$ , 171. Reflectance spectra were measured using a Beckman DU spectrophotometer with the standard Beckman reflectance accessory and magnesium carbonate as the reference solid. A Gary Model 14 recording spectrophotometer was used to obtain solution spectra and the spectra of crystals milled in hexachlorobutadiene and Nujol.

- (1) (a) Alfred P. Sloan Foundation Fellow. (b) Department of Chemistry, Imperial College of Science and Technology, London. (c) Northampton College of Advanced Technology, London.
- (2) Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, **9**, 753 (1954).
- (3) L. E. Orgel, *J. Chem. Phys.*, **23**, 1004 (1955).
- (4) C. K. Jørgensen, *Acta Chem. Scand.*, **8**, 1502 (1954).
- (5) C. K. Jørgensen, *ibid.*, **11**, 53 (1957).
- (6) L. J. Heidt, G. F. Koster and A. M. Johnson, *J. Am. Chem. Soc.*, **80**, 6471 (1958).
- (7) J. W. Stout, *J. Chem. Phys.*, **31**, 709 (1959).
- (8) R. Pappalardo, *ibid.*, **33**, 613 (1960).
- (9) H. P. de la Garanderie and D. Curie, *Compt. rend.*, **248**, 3151 (1959).
- (10) F. S. Taylor, *J. Chem. Soc.*, **20**, 699 (1934).
- (11) L. Naldini and A. Sacco, *Gazz. chim. ital.*, **89**, 2258 (1959).
- (12) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).
- (13) D. M. L. Goodgame and F. A. Cotton, *ibid.*, 3735 (1961).
- (14) S. Buffagni and T. M. Dunn, *Nature*, **188**, 937 (1960).
- (15) See H. W. Leverenz, "An Introduction to Luminescence of Solids," John Wiley and Sons, Inc., New York, N. Y., 1950, and F. A. Kröger, "Inorganic Crystal Phosphors" in *Ergebnisse der Exakten Naturwissenschaften*, Bd. 29, Springer-Verlag, Berlin, 1956, p. 61.

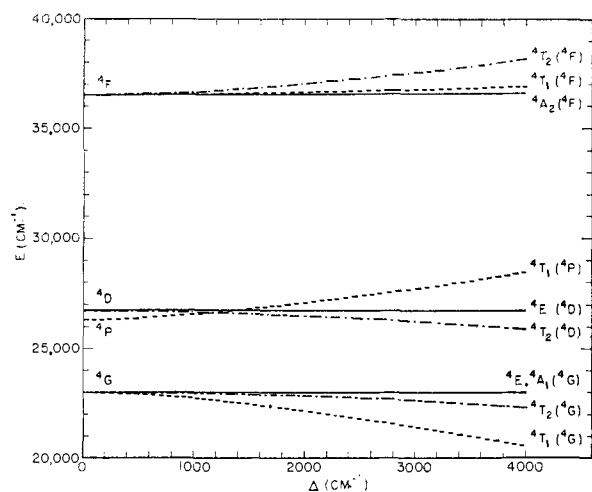


Fig. 1.—Energy level diagram for the quartet states of the manganese(II) ion in  $[\text{MnBr}_4]^{2-}$ . Energies are referred to the energy of the  ${}^6\text{A}_1$  ground state as zero. Details of the procedure for obtaining this diagram are described in the text.

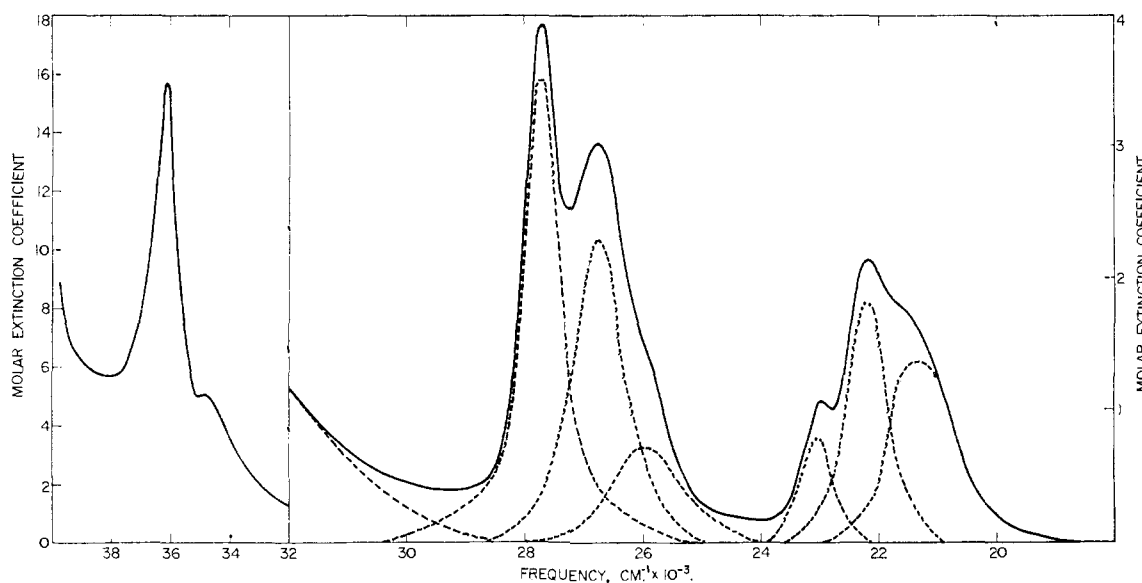


Fig. 2.—The observed spectrum of the  $[\text{MnBr}_4]^{2-}$  ion, measured at  $25^\circ$  using a  $0.1\text{ M}$  solution of  $(\text{Et}_4\text{N})_2[\text{MnBr}_4]$  in acetonitrile. The dotted lines show a trial and error resolution of the two groups of bands at lower energies into overlapping Gaussian curves.

### Discussion

The salts studied are, like all other tetrahedral manganese(II) complexes reported, pale green, yellow or yellow-green in color; larger crystals are more markedly colored while very fine powders often appear practically colorless. This green, yellow or yellow-green color seems to afford a simple and reliable criterion for recognizing tetrahedral, as opposed to octahedral, manganese(II) complexes, since the latter have very pale red or pink tints.

All of the tetrahalomanganate(II) complexes described here showed a marked, yellow-green fluorescence under ultraviolet light. However, solutions of the compounds showed no fluorescence. Methyltriphenylphosphonium tetrachloromanganate(II) and tetraethylammonium tetrabromoman-

ganate(II) displayed triboluminescence, emitting yellow-green light when rubbed with a glass rod. The tetraiodomanganate(II) and the other tetrachloromanganate(II) complexes did not show this effect. Similar effects have been reported by the present authors<sup>13</sup> for the tetrahedral manganese(II) complexes of the types  $[\text{Mn}((\text{C}_6\text{H}_5)_3\text{PO})_2\text{X}_2]$  and  $[\text{Mn}((\text{C}_6\text{H}_5)_3\text{AsO})_2\text{X}_2]$ . These luminescence effects also seem to be diagnostic of tetrahedrally coordinated Mn(II), although their absence cannot be considered as evidence against tetrahedral coordination of Mn(II).

The molar conductances in nitromethane are within the normal ranges for 1–2 electrolytes in this solvent and thus support the proposed structural formulations.

All of the spectral data are collected in Table I. As in previous studies of the spectra of tetrahedral tetrahalo complexes of Ni(II)<sup>16</sup> and Co(II),<sup>17</sup> it was found that the spectra of solutions were subject to solvolysis effects of varying magnitude (sometimes negligible) which could be eliminated by addition of a salt of the halide occurring in the complex. This was particularly true of the  $[\text{MnI}_4]^{2-}$  com-

pounds. It seems to be generally true that for a given metal, M, it is the  $[\text{MI}_4]^{2-}$  species which is most sensitive to solvent effects.

Qualitative interpretation of the  $[\text{MnX}_4]^{2-}$  spectra is possible without difficulty. Figure 1 shows an energy level diagram for  $[\text{MnBr}_4]^{2-}$  in which the energies of all of the quartet states, relative to the energy of the  ${}^6\text{A}_1$  ground state, are plotted vs.  $\Delta$  for values of 0 to  $4000\text{ cm}^{-1}$  in the latter parameter. The way in which this diagram was constructed will be discussed in detail later. Figure 2 shows the observed spectrum of the  $[\text{MnBr}_4]^{2-}$  ion.

(16) D. M. L. Goodgame, M. Goodgame and F. A. Cotton, *J. Am. Chem. Soc.*, **83**, 4161 (1961).

(17) F. A. Cotton, D. M. L. Goodgame and M. Goodgame, *ibid.*, **83**, 4690 (1961).

TABLE I  
 ELECTRONIC ABSORPTION SPECTRA OF THE COMPLEXES

Compound	State	Position of absorption bands $\text{cm.}^{-1}$ (molar extinction coefficients for solutions)						High energy bands			
		${}^4\text{T}_1(^4\text{G})$	${}^4\text{T}_2(^4\text{G})$	${}^4\text{E}(^4\text{G})$	${}^4\text{A}_1(^4\text{G})$	${}^4\text{T}_2(^4\text{D})$	${}^4\text{E}(^4\text{D})$	${}^4\text{T}_1(^4\text{P})$			
$(\text{PyH})_2(\text{MnCl}_4)$	Reflectance	21,050(sh)	22,000	23,000		26,200	27,600	<sup>a</sup>			
	Hexachlorobutadiene mull	21,280(sh)	22,270	23,090	23,200	26,110	27,030	27,860			
	Dimethylformamide (0.2 M)	<sup>b</sup>	22,500(1.29)	23,300(1.18)	23,600		27,000(sh)	28,090(2.75) <sup>c</sup>			
$(\text{Me}(\text{C}_6\text{H}_5)_2\text{P})_2(\text{MnCl}_4)$	Reflectance	21,050(sh)	22,320	23,040		26,670(?)		27,780			
	Nujol mull	21,300(br,sh)	22,400	23,150	23,300	26,500(sh)	27,000(sh)	28,000			
	$\text{CH}_3\text{CN}$ (0.1 M)	21,500(br,sh)	22,400(0.75)	23,150(0.55)	23,360(sh)	26,400(sh)	27,100(sh)	28,000(1.15)			
	0.1 M $(\text{Me}(\text{C}_6\text{H}_5)_2\text{P})\text{Cl}$ in $\text{CH}_3\text{CN}$ (0.05 M)	21,400(br,sh)	22,470(0.9)	23,200(0.7)	23,470(sh)	26,390(sh)	27,170(sh)	28,010(1.4)			
$(\text{Me}_4\text{N})_2(\text{MnCl}_4)$	Reflectance	21,300(sh)	22,200	23,000		26,700(sh)		27,800			
	Hexachlorobutadiene mull	21,200(br,sh)	22,370	23,090	23,360(sh)	26,250(sh)	27,030(sh)	27,930			
	Nujol mull		22,320	23,040	23,310(sh)	26,200(sh)	26,810	27,930	35,700(sh) <sup>c</sup>	38,000(sh) <sup>c</sup>	
$(\text{Et}_4\text{N})_2(\text{MnBr}_4)$	Reflectance	20,830(sh)	21,830	22,990		26,320					
	Hexachlorobutadiene mull	21,180	22,030	22,880(sh)	23,810(sh)	25,910(sh)	26,600	27,620			
	Nujol mull	21,460(br,sh)	22,170	22,940		25,800(sh)	26,600	27,600	33,300	35,150	37,450
	$\text{CH}_3\text{CN}$ (0.1 M)	21,300(sh)	22,170(2.1)	22,990(1.2)		25,840(sh)	26,740(2.9)	27,700(3.7)	34,720 <sup>c</sup>	36,100 <sup>c</sup>	
	$\text{CH}_3\text{CN}$ saturated with $(\text{Et}_4\text{N})\text{Br}$ (0.1 M)	21,370(sh)	22,170(2.0)	22,990(1.0)		25,840(sh)	26,740(2.8)	27,700(3.7)	34,600 <sup>c</sup>	36,200 <sup>c</sup>	
	Dimethylformamide (0.1 M)	21,500(br,sh)	22,300(1.3)	23,100(0.7)		25,840(sh)	26,800(1.5)	27,800(2.4)			
	Dimethylformamide saturated with $(\text{Et}_4\text{N})\text{Br}$ (0.1 M)	21,370(sh)	22,270(1.5)	23,090(0.7)		25,840(sh)	26,700(1.7)	27,740(2.6)			
	$\text{CH}_3\text{NO}_2$ (0.1 M)	21,400	22,200(2.1)	23,000(1.2)		25,840(sh)					
	Reflectance	21,140		22,220(sh)		25,700	26,600	28,200(sh)	31,950	33,060	34,480
	Hexachlorobutadiene mull	21,500		22,520		26,186(sh)	26,880	27,800(sh)			
$(n\text{-Bu}_4\text{N})_2(\text{MnI}_4)$	Nujol mull	21,410(sh)		22,310		25,840	26,900	28,000(sh)	32,260(sh)	33,560	36,000
	$\text{CH}_3\text{CN}$ (0.02 M)	21,410(11.1)		22,600(5.6)		25,770(sh)	26,460(sh)	27,320(28.8)	33,220(sh)		35,100 <sup>c</sup>
	1.0 M $(n\text{-Bu}_4\text{N})\text{I}$ in $\text{CH}_3\text{CN}$ (0.02 M)	21,410(15.3)		22,420(sh)		26,180(55)	26,880(56.6)	28,170(sh)	32,900(sh)		
	Acetone (0.02 M)	21,500(10)		22,700(sh)		26,100(br,sh)	27,300(27.1)				
	0.5 M $(n\text{-Bu}_4\text{N})\text{I}$ in acetone (0.02 M)	21,460(15.3)		22,470(sh)		26,250(59)	26,950(61.7)	28,170(sh)			
	$\text{CH}_2\text{Cl}_2$ (0.02 M)	21,300(13.3)		22,300(sh)		25,906(31.8)	26,700(29)		32,500(sh) <sup>c</sup>		
	0.5 M $(n\text{-Bu}_4\text{N})\text{I}$ in $\text{CH}_2\text{Cl}_2$ (0.02 M)	21,320(15.0)		23,320(sh)		26,180(55.4)	26,810(57.5)	28,100(sh)	32,800(sh)		
	$\text{CHCl}_3$ (0.01 M)	21,600(10)		22,830(8.4)		25,770(sh)	27,170(62)				
	0.5 M $(n\text{-Bu}_4\text{N})\text{I}$ in $\text{CHCl}_3$ (0.02 M)	21,320(15.3)		22,370(sh)		26,180(sh)	26,810(74.1)	28,100(sh)			
	$\text{CH}_3\text{NO}_2$ (0.02 M)	21,400(13.1)		22,300(6.8)							

<sup>a</sup> Charge transfer band commences  $\sim 28,600 \text{ cm.}^{-1}$ . <sup>b</sup> Band of  ${}^4\text{T}_2(^4\text{G})$  transition broad towards low energy side, probably concealing shoulder due to  ${}^4\text{T}_1(^4\text{G})$ . <sup>c</sup> On side of steeply rising charge transfer band.

The energy level diagram indicates that a closely spaced group of three absorption bands, caused by transitions to the states originating from the  ${}^4G$  term of the free ion, should be found in the range 20,000 to 25,000  $\text{cm}^{-1}$ . This group of bands is clearly seen in Fig. 2, where we also have shown how the observed envelope can be resolved into three approximately Gaussian bands. In making such a Gaussian analysis of the observed absorption, it turns out quite naturally that the uppermost band in this group appears to be definitely narrower than the other two. As Orgel<sup>18</sup> has shown, this is to be expected since the upper,  ${}^4E, {}^4A_1({}^4G)$ , and lower,  ${}^6A_1$ , states concerned in this uppermost band have the same slopes on the energy level diagram, whereas the other two bands involve excited states with slopes different from that of the ground state. For octahedral complexes, such as the  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  ion, a significant difference in the widths of the other two bands is also observed, the lower one being the broader as the energy level diagram requires. As Fig. 2 shows, the  $[\text{MnBr}_4]^{2-}$  spectrum can be resolved so as to make the lowest band somewhat broader than the middle one, but because of the inherent uncertainty in the resolution procedure, it cannot be said that such a result is rigorously required. At the low  $\Delta$  values prevailing in the tetrahedral complexes, the difference in the slopes of the  ${}^4T_1(G)$  and  ${}^4T_2(G)$  states is less than it is at the higher  $\Delta$  values found in octahedral complexes, so that we do not in fact expect the difference in band widths to be as great.

The energy level diagram shows that the next absorption bands should be another closely spaced group of three in the range 25,000 to 28,000  $\text{cm}^{-1}$ , and this group is clearly evident in Fig. 2. Again, the figure indicates a Gaussian analysis of the observed envelope, but, in this case, the overlapping of the bands is so severe that no reliable conclusions as to relative band widths are possible. Thus, we are denied any simple means of assigning the  ${}^6A_1 \rightarrow {}^4E(D)$  transition, which should have the narrowest band. This causes some difficulty when a quantitative interpretation is attempted, as will be seen later.

Finally, the spectrum should contain a third set of three bands in the region 36,000 to 38,000  $\text{cm}^{-1}$  due to transitions to the states arising from the  ${}^4F$  term. These transitions are less easily observed than the six already discussed because they occur in a region where solvent absorption, absorption by some of the organic groups in the cations and charge transfer absorption by the  $[\text{MX}_4]^{2-}$  complexes themselves become prominent and tend to obscure the relatively weak d-d bands. In all three of the  $[\text{MnX}_4]^{2-}$  species a band we can assign to the  ${}^6A_1 \rightarrow {}^4A_2({}^4F)$  transition has been observed and there is some indication of the  ${}^6A_1 \rightarrow {}^4T_2({}^4F)$  transition for  $[\text{MnBr}_4]^{2-}$ . Other small bands or shoulders have been observed from 32,000 to 35,000  $\text{cm}^{-1}$  which, for reasons which are explained later, we prefer to assign to transitions having doublet upper states.

(18) For discussion and references see L. E. Orgel, "An Introduction to Transition Metal Chemistry," Methuen and Co., Ltd., London, 1960

For the  $[\text{MnCl}_4]^{2-}$  and  $[\text{MnI}_4]^{2-}$  ions, the experimental observations were much the same, differing in no essential way from those described for the  $[\text{MnBr}_4]^{2-}$  ion, and the qualitative features of the assignments we have made are therefore also essentially the same. It is interesting to note that for  $[\text{MnCl}_4]^{2-}$  we observe a small splitting in the uppermost band of the low energy triplet (at  $\sim 23,200 \text{ cm}^{-1}$ ). Since we assign the corresponding unsplit band in  $[\text{MnBr}_4]^{2-}$  to the transition to the accidentally degenerate  ${}^4E({}^4G)$  and  ${}^4A_1({}^4G)$  states, the splitting observed in the spectrum of  $[\text{MnCl}_4]^{2-}$  can be readily explained as due to a slight resolution of this degeneracy, as is observed in various octahedral species, e.g.,  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ . The observation of this splitting provides good evidence for the essential correctness of our assignments in the low energy triplet since other assignments (for example, assuming a large  ${}^4E({}^4G) - {}^4A_1({}^4G)$  splitting in all cases and assuming that the transition to either  ${}^4T_1({}^4G)$  or  ${}^4T_2({}^4G)$  is weak and unobserved) afford no convenient explanation for this splitting.

For all three  $[\text{MnX}_4]^{2-}$  ions the intensities of the bands are markedly greater than for octahedral complexes. They are, in fact, in accord with the apparently general ratio of approximately  $10^2$  between the intensities of bands in the tetrahedral and octahedral complexes of other metal ions, such as  $\text{Co(II)}$ <sup>17</sup> and  $\text{Ni(II)}$ .<sup>16</sup> It is noteworthy, however, that the band intensities in the  $[\text{MnI}_4]^{2-}$  spectrum are significantly greater, by a factor of 5 to 10, than those in the  $[\text{MnCl}_4]^{2-}$  and  $[\text{MnBr}_4]^{2-}$  spectra.

In attempting to account quantitatively for the spectral data for the  $[\text{MnX}_4]^{2-}$  ions, we have been guided by the published studies of the spectra of octahedral  $\text{Mn(II)}$  complexes, particularly by the work of Heidt, Koster and Johnson<sup>6</sup> (hereafter HKJ) on the  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  spectrum. HKJ found that using only the parameters B, C and  $\Delta$  they obtained the best fit to the data on  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  by assigning these the values 671, 3710 and 8480  $\text{cm}^{-1}$  respectively. Two comments on their work should be made before turning to our analysis of the  $[\text{MnX}_4]^{2-}$  spectra. (1) Although HKJ's calculated band energies agree with the observed ones within, on the average, 5% of the total energies, the errors constitute much larger percentages of the differences in energies of the upper states among themselves. (2) The treatment of the term separations using only the two Racah parameters gives a very poor prediction of the position of the  ${}^4P$  term of the free ion ( $\sim 8.75\%$  too high) and of the  ${}^4T_1(P)$  state of the  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  ion ( $\sim 5.7\%$  too high).

The energy level diagram for the  $[\text{MnBr}_4]^{2-}$  ion, which is shown in Fig. 1, was constructed in the following way. The assignment of the three bands in the 25,000 to 28,000  $\text{cm}^{-1}$  region could be made in one of the following three ways, where we list the upper states in order of decreasing energy: (1)  ${}^4T_1(P), {}^4E(D), {}^4T_2(D)$ ; (2)  ${}^4E(D), {}^4T_1(P), {}^4T_2(D)$ ; (3)  ${}^4E(D), {}^4T_2(D), {}^4T_1(P)$ . Assignment 2 can be eliminated immediately since the  ${}^4E(D) - {}^4T_2(D)$  separation would require a  $\Delta$  value twice as great as the  $\Delta$  value suggested by the separations in the states arising from the  ${}^4G$  term. Assignment 3 was then eliminated in favor of (1) because from the

TABLE II  
COMPARISON OF OBSERVED AND CALCULATED ABSORPTION MAXIMA (CM.<sup>-1</sup>) AND THE ELECTRONIC STRUCTURE PARAMETERS (CM.<sup>-1</sup>) USED<sup>a</sup>

Upper states of absorptions and parameters used	[MnBr <sub>4</sub> ] <sup>2-</sup>		Complex [MnCl <sub>4</sub> ] <sup>2-</sup>		[MnI <sub>4</sub> ] <sup>2-</sup>	
	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.
<sup>4</sup> T <sub>1</sub> (G)	21,300	21,350	21,300	21,200	.... <sup>b</sup>	
<sup>4</sup> T <sub>2</sub> (G)	22,600	22,180	22,700	22,400	.... <sup>b</sup>	21,500
<sup>4</sup> E, <sup>4</sup> A <sub>1</sub> (G)	(23,000)	(23,000)	(23,200)	(23,200)	(22,500)	(22,500)
<sup>4</sup> T <sub>2</sub> (D)	26,200	25,900	26,400	26,300	.... <sup>b</sup>	26,000
<sup>4</sup> E(D)	(26,750)	(26,750)	(27,100)	(27,100)	(26,900)	(26,900)
<sup>4</sup> T <sub>1</sub> (P)	27,750	27,700	28,800	27,900	.... <sup>b</sup>	28,100
<sup>4</sup> A <sub>2</sub> (F)	36,500	36,150	38,000	~38,000	37,400	~36,000
<sup>4</sup> T <sub>1</sub> (F)	36,700	36,150	38,300	Not obsd.	.... <sup>b</sup>	Not obsd.
<sup>4</sup> T <sub>2</sub> (F)	37,500	~37,400	39,300	Not obsd.	.... <sup>b</sup>	Not obsd.
B	536	....	558	....	667	....
C	3,530	....	3,524	....	3,250	....
Δ	3,100	....	3,600	....	Not calcd. <sup>b</sup>	....

<sup>a</sup> Energies in parentheses are field-strength-independent ones which were used to assess *B* and *C*. <sup>b</sup> As explained in the text, the data are insufficient to permit any reliable estimate of Δ.

positions of the <sup>4</sup>E(D) and <sup>4</sup>E(G) states in assignment 3 one obtains a *B* value of 671 cm.<sup>-1</sup> and a *C* value of 3257 cm.<sup>-1</sup>. This seems unlikely when compared with the *B* and *C* values obtained by HKJ for [Mn(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>, since it means that the entire difference between [MnBr<sub>4</sub>]<sup>2-</sup> and [Mn(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> is in *C* with no difference in *B*. Assignment 1, however, gives a *B* value of 536 cm.<sup>-1</sup> and a *C* value of 3530 cm.<sup>-1</sup>, both lower, by about the same fraction, than those for the [Mn(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> ion.

Having selected this assignment, the *B* and *C* values were used to calculate the positions of the free ion terms for Δ equal to zero. The energy of the <sup>4</sup>P term of the ion in zero field then was lowered by 7.5%. An arbitrary value of *C*, chosen so as to fit this placement of the <sup>4</sup>G, <sup>4</sup>P and <sup>4</sup>F terms relative to one another (but not their absolute placement) then was used, together with the *B* value derived from the <sup>4</sup>E(D)-<sup>4</sup>E(G) separation, in the secular equations of Tanabe and Sugano<sup>2</sup> for the <sup>4</sup>T<sub>1</sub> and <sup>4</sup>T<sub>2</sub> levels. These equations were solved for Δ values of 1000, 2000, 3000 and 4000 cm.<sup>-1</sup>. By this procedure the relative energies of the states arising from the quartet terms of the free ion were obtained to a good approximation. Their absolute positions relative to the ground state then were determined using the exact *B* and *C* values given by the energies of the <sup>4</sup>A<sub>1</sub> → <sup>4</sup>E, <sup>4</sup>A<sub>1</sub>(<sup>4</sup>G) and <sup>4</sup>A<sub>1</sub> → <sup>4</sup>E(<sup>4</sup>D) transitions. The experimental results are compared with those which can be read from the energy level diagram for Δ equal to 3100 cm.<sup>-1</sup> in Table II.

For [MnCl<sub>4</sub>]<sup>2-</sup>, quantitative treatment of the data was carried out in the same fashion and the results are recorded in Table II.

With [MnI<sub>4</sub>]<sup>2-</sup>, serious difficulties were encountered and quantitative treatment could not be carried out to any significant extent. Poor resolution makes it impossible to assign enough of the proper low energy bands to permit any meaningful assessment of the Δ value. Values of *B* and *C* were obtained from the energies of bands to which <sup>4</sup>E, <sup>4</sup>A<sub>1</sub>(<sup>4</sup>G) and <sup>4</sup>E(<sup>4</sup>D) were assigned as upper states. From these, the position of the band with the <sup>4</sup>A<sub>2</sub>(F) upper state was predicted in fair agreement with an observed absorption band.

**Conclusions.**—Aside from the qualitative conclusions as to general regions of absorption and the

intensities of the bands, which already have been noted, several aspects of the quantitative treatment of the data merit comment.

The manner in which the position of the <sup>4</sup>P state has been manipulated is empirically and not theoretically dictated. However, from a theoretical viewpoint, it is not without plausibility. Our treatment merely amounts to introducing a third adjustable parameter in addition to *B* and *C*, and it cannot be considered surprising, or indeed unlikely, that only two interelectronic repulsion parameters fail to fix precisely the relative energies of all five terms.

It is also necessary to point out explicitly that we have chosen to assume that those higher energy absorptions which fall below the calculated energies of the <sup>6</sup>A<sub>1</sub> → <sup>4</sup>A<sub>2</sub>(<sup>4</sup>F) transitions are either extraneous or are due to transitions having doublet upper states. The alternative would be to assume that the calculation of the energy of the <sup>4</sup>F term using *B* and *C* values obtained from the energies of the <sup>4</sup>G and <sup>4</sup>D terms is very seriously in error. On the basis of the successful results which have been obtained for the free ion<sup>6</sup> and for octahedral Mn(II),<sup>6-8</sup> this seems the more unlikely contingency. In their treatment of [Mn(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>, HKJ explicitly suggested that a weak band at 26,500 cm.<sup>-1</sup> is due to a transition with a doublet upper state, and their spectrum also contains one, and perhaps two, other weak shoulders which cannot be assigned in any other way. It may be seen in Fig. 2 that the band at 36,100 cm.<sup>-1</sup> in [MnBr<sub>4</sub>]<sup>2-</sup> is about as narrow as those corresponding to the other transitions with horizontal upper states.

The values of Δ obtained for [MnCl<sub>4</sub>]<sup>2-</sup> and [MnBr<sub>4</sub>]<sup>2-</sup> are in accord with the accepted positions of Cl<sup>-</sup> and Br<sup>-</sup> in the spectrochemical series.<sup>19</sup> The spectral data for these two complexes also show that Br<sup>-</sup> is more nephelauxetic than is Cl<sup>-</sup> in agreement with the accepted order.<sup>19</sup> While there is not a great deal of information available on the position of the iodide ion in the nephelauxetic series, the results of our spectra studies<sup>16,17</sup> of the [CoX<sub>4</sub>]<sup>2-</sup> and [NiX<sub>4</sub>]<sup>2-</sup> ions led to the conclusion

(19) See T. M. Dunn in "Modern Coördination Chemistry," J. Lewis and R. G. Wilkins, Editors, Interscience Publishers, New York, N. Y., 1960, for discussion and references.

that it is probably somewhat more nephelauxetic than  $\text{Cl}^-$  or  $\text{Br}^-$ . The present data on  $[\text{MnCl}_4]^{2-}$  are too limited and inaccurate to offer any definite evidence on this point.

There is a notable discrepancy between our  $\Delta$  value of  $\sim 3600 \text{ cm.}^{-1}$  and Buffagni and Dunn's value<sup>14</sup> of  $2650 \text{ cm.}^{-1}$  for the  $[\text{MnCl}_4]^{2-}$  ion. So large a discrepancy obviously requires comment. First, it should be emphasized that the difference in  $\Delta$  values is due entirely to a difference in interpretation of data; there are no significant differences between Dunn's data and ours. It also should be noted that the exact numerical value of  $\Delta$  is of somewhat limited significance, since it is impossible, within the theoretical framework of the Tanabe and Sugano treatment, to obtain perfect agreement between calculated and observed energies of the lower six transitions for any reasonable  $\Delta$  value. This is because the ratio of the separations  ${}^4\text{T}_2({}^4\text{G})$ – ${}^4\text{T}_1({}^4\text{G})$  and  ${}^4\text{E}, {}^4\text{A}_1({}^4\text{G})$ – ${}^4\text{T}_2({}^4\text{G})$  is theoretically of the order of  $\sim 3$  throughout the range of  $\Delta$  from 1000 to  $4000 \text{ cm.}^{-1}$  (see Fig. 1), whereas, experimentally, this ratio is  $\sim 1$ . Finally, it also must be recognized that the slopes of the energy lines for all of the lower states, on which the evaluation of  $\Delta$  depends, are not great, so that the sum of squares of deviations has no pronounced minimum in the range of reasonable  $\Delta$  values. The center of the broad shallow minimum is, however, at  $\sim 3600 \text{ cm.}^{-1}$ . The sum of squares of deviations at  $\Delta = 2650 \text{ cm.}^{-1}$  is about two times greater than at  $\Delta = 3600 \text{ cm.}^{-1}$ .

As a form of independent support for a  $\Delta$  value of  $\sim 3600 \text{ cm.}^{-1}$  in preference to one of  $\sim 2600 \text{ cm.}^{-1}$ , we have made a comparison of  $\Delta$  values for  $[\text{MnCl}_4]^{2-}$ ,  $[\text{CoCl}_4]^{2-}$  and  $[\text{NiCl}_4]^{2-}$  with those for the corresponding hexa-aquo ions, which Buffagni

and Dunn regarded as offering support for their results. Their results and ours for the  $[\text{CoCl}_4]^{2-}$  and  $[\text{NiCl}_4]^{2-}$  systems have previously been shown to be in satisfactory agreement.<sup>16,17</sup>  $\Delta$  values for the aquo ions have been taken from the sources noted in Table III. It can be seen that, with  $\Delta$  equal to  $\sim 3600 \text{ cm.}^{-1}$  for  $[\text{MnCl}_4]^{2-}$ , the  $\Delta_t/\Delta_0$  ratio for Mn(II) is within 4% of the average value of this ratio for Co(II) and Ni(II) while with  $\Delta$  equal to  $2650 \text{ cm.}^{-1}$ , the ratio is 25% lower.

TABLE III  
COMPARISON OF  $\Delta$  VALUES IN  $[\text{MCl}_4]^{2-}$  AND  $[\text{M}(\text{H}_2\text{O})_6]^{2+}$   
SPECIES FOR M = Mn, Co AND Ni

Metal	$\Delta_0$ in $[\text{M}(\text{H}_2\text{O})_6]^{2+}$	$\Delta_t$ in $[\text{MCl}_4]^{2-}$	$\Delta_0/\Delta_t$
Mn	8500 <sup>a</sup>	2650 <sup>d</sup>	0.312
		3600 <sup>e</sup>	.423
Co	8300 <sup>b</sup>	3200 <sup>f</sup>	.386
Ni	8500 <sup>c</sup>	3625 <sup>g</sup>	.427

<sup>a</sup> From ref. 6. <sup>b</sup> Obtained from the results of C. J. Ballhausen and C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 397 (1955), using an energy level diagram computed by A. D. Liehr from the complete matrices of J. C. Eisenstein, *J. Chem. Phys.*, **34**, 1628 (1961); A. D. Liehr, private communication, presented in part at the Symposium on Molecular Structure and Spectroscopy, Ohio State University, Columbus, Ohio, June 12–16, 1961 (to be submitted to *J. Phys. Chem.*). <sup>c</sup> From A. D. Liehr and C. J. Ballhausen, *Ann. Phys. (N. Y.)*, **6**, 134 (1959). <sup>d</sup> From ref. 14. <sup>e</sup> Present work. <sup>f</sup> Average of values in ref. 14 and 17. <sup>g</sup> Average of values in ref. 14 and 16.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ISRAEL INSTITUTE OF TECHNOLOGY, HAIFA, ISRAEL]

## Intramolecular Energy Transfer in a Naphthalene–Anthracene System

BY O. SCHNEPP AND M. LEVY

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Intramolecular energy transfer has been demonstrated in three homologous 9-anthryl-1'-naphthyl-alkanes in which the anthracene and naphthalene units were joined by saturated chains of 1, 2 and 3 carbon atoms. The absorption spectra of these compounds bear evidence that the two aromatic  $\pi$ -electron systems do not overlap appreciably. The naphthalene group of the compound molecule was excited by appropriately filtered radiation and the resulting fluorescence was characteristic of the anthracene group. From the comparative fluorescence intensity measurements relative as well as absolute values of the quantum efficiencies of the energy transfer process were calculated. The relative fluorescence quantum yields were also obtained.

### Introduction

The absorption spectrum of naphthalene<sup>1</sup> begins at  $3100 \text{ \AA.}$  with a very weak absorption system ( $\epsilon = 200$ ) which fuses into a much stronger system with maximum at  $2770 \text{ \AA.}$  ( $\epsilon = 5000$ ) and a very intense absorption band appears at  $2200 \text{ \AA.}$  ( $\epsilon = 10^5$ ). The absorption spectrum of anthracene<sup>1</sup> begins with a medium absorption at  $3750 \text{ \AA.}$  ( $\epsilon = 8000$ ) and has a very intense peak at  $2530 \text{ \AA.}$  ( $\epsilon = 1.6 \times 10^5$ ). It is clear from these data that

the intense peaks of these two compounds do not overlap and it should therefore be possible to excite one of the substances by irradiation in the presence of the other. This is only approximately true, however, since the absorption coefficient of anthracene at  $2800 \text{ \AA.}$  still has a finite value, even though it is much smaller than that of naphthalene at this wave length.

It was believed that in view of the discussion of the last paragraph a molecule consisting of non-conjugated anthracene and naphthalene units would be very suitable for a study of intramolecular energy transfer. Such molecules were synthe-

(1) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951.