YU ISSN 0015—3206
FZKAAA 17 (1) 27 (1985)

OPTICAL CHARACTERIZATION OF TETRAHALOMANGANATES AND OTHER MANGANESE COMPLEXES CONTAINING IODINE

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Received 18 July 1984

UDC 538.958

Original scientific paper

Shifts of the emission spectra between chlorine, bromine and iodine containing complexes are found to be hardly larger than temperature shifts, and definitely smaller than some *accidental* shifts as due for instance to the degree of hydratation of the material. On the other hand, the decrease of Racah parameters B and C, as given by absorption/excitation spectra, behaves as expected from elementary covalency considerations. The behaviour of the ratio C/B when the Mn^{2+} ions are embedded into the complexes shows an enhancement of the Trees parameter α, the magnitude of which depends mainly on the distorsion of the ligand structure from the regular tetrahedron or octahedron.

1. Introduction

Tetrahalomanganates complexes containing MnX_4^{2-} (X= Cl or Br) have been extensively studied during the past 20 years. On the other hand, complexes with X = I are often unstable and the preparation of the pure compound is usually

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more difficult. For instance Wrighton and Ginley[1] performed a comparative study of optical spectra and mean lives in 11 complexes, but only one example is given which permits to follow the whole series MnX_4^{2-} with X = Cl, Br and I by using the same organical basis in the three complexes:

TABLE 1

Compound	300 K	77 K
$(Me_4)_2\ MnCl_4$	19 000 cm^{-1}	18 900 cm^{-1}
$(Me_4N)_2\ MnBr_4$	19 000 cm^{-1}	18 800 cm^{-1}
$(Me_4N)_2\ MnI_4$	18 800 cm^{-1}	18 400 cm^{-1}

Emission peaks according to Ref. 1.

As a general rule, the peak positions of emission spectra of X = Cl and Br do not differ very much, while the peak position for X = I occurs at a lower energy as a result of increased covalency in these materials.

However the purpose of this paper is to show that this »rule« must be considered with some suspicion. Moreover, a mere determination of the emission spectrum is not sufficient for the characterization of X, the absorption (or excitation) spectrum — and specifically the position of the $^6A_{1g} \rightarrow 4E_g$ transitions when they can be unambigously identified — leads to a much better characterization.

2. *Experimental*

2.1. *Tetrahalomanganates.* — Some results on complexes made of pyridinium ions are given in Table 2:

TABLE 2.

Compound	Emission peak	Excitation bands				
		$^4T_1\ (^4G)$	$^4T_2\ (^4G)$	$^4E\ (^4G)$	$^4T_2\ (^4D)$	$^4E\ (^4G)$
$(C_5H_5NH)_2\ MnCl_4$	19 120 300K 19 075 4 K	21.050	22.220	23.006	25.925	27.670 at 4 K
$(C_5H_5NH)_2\ MnBr_4$	19 300 300 K 19 100 4 K	20.830	21.970	22.880	26.280	27.380 at 4 K
$(C_5H_5NH)_2\ MnI_4$	18 605 300 K	?	21.200	22.220	?	? at 300 K (*)

* The iodine compound shows very broad and flat bands, their structures and peak positions cannot be unambigously identified.

Position of bands in cm^{-1}.

The figures which are given here are in reasonable agreement with those given by previous authors[2,3]. All data above are relevant with the position of the center gravity of the bands, *not* the zero phonon lines. It has been shown indeed by Williams and Curie[4] that the center of gravity of the bands must be taken into account for an adequate application of conventional Tanabe-Sugano theory of crystal field effects.

It is seen, that the energy of the $^4E(^4G)$ level decays regularly from X = Cl to X = Br and eventually X = I, while the shift of emission occurs in the oposite direction if we compare bromine to chlorine. This result is connected with a larger Stokes' shift in the bromine compound. Thus this behaviour of the emission peak is just the reverse of the naive conclusions expected from covalency effects.

Triphenylmethylarsonium compounds are of special interest because the site symmetry was shown to be quite near a regular tetrahedron[5]. The crystals of triphenylmethylarsonium halogenates complexes are easily prepared by using stoichiometric amounts of triphenylmethylarsonium halides on the one hand, and of the corresponding manganese (II) halides on the other hand. Both materials are dissolved in methanol. After a few days at room temperature, regular crystals of the complex are being deposited.

Our results are as follows:

TABLE 3.

Compound	Emission peak at 300 K	Excitation bands at 4 K				
		$^4T_1(^4G)$	$^4T_2(^4G)$	$^4E(^4G)$	$^4T_2(^4D)$	$^4E(^4D)$
$[(MePh_3)As]_2MnCl_4$	19.575	?	22.400	23.200	26.660	27.855
$[(MePh_3)As]_2MnI_4$	19.250	?	?	22.880	26.455	27.470
$[(MePh_3)As]_2MnI_4$	19.100	?	?	22.220	25.380	26.740

Position of bands in cm^{-1}.

Here the shift of the emission spectrum occurs in the same direction as the shift of excitation bands all along the series, however we observe that the difference between the emission peaks for X = Cl and X = Br is greater than the difference between X = Br and X = I, while the $^4E(^4G)$ and $^4E(^4D)$ levels behave as expected from covalency (Fig. 1).

2.2. *Octahedral coordination* — Approximate positions of the $^6A_1(^6S) \rightarrow {}^4E(^4G)$ band for halogen ligands have been given by Jørgensen[6]:

MnF_2 25.300 cm^{-1}; $MnCl_2$ 23.700 cm^{-1}; MnBr 23.300 cm^{-1};

MnI_2 22.400 cm^{-1}

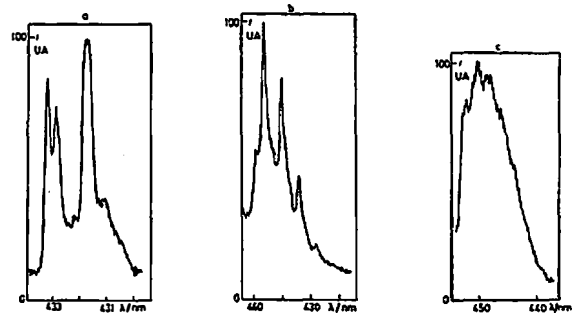

Fig. 1. The $^6A_1$ (^6S) → ^4E (^4G) excitation band in triphenylmethylarsonium tetrahalomanganates.
a) X = Cl; b) X = Br; c) X = I.

in octahedral coordination. It is of interest to compare these values to those obtained in tetrahedral coordination, which lie usually in the range:

$$MnCl_4^{2-}\ 23.100—23.300\ cm^{-1};\quad MnBr_4^{2-}\ 22.800—23.000\ cm^{-1}$$
$$MnI_4^{2-}\ 22.200—22.500\ cm^{-1}$$

depending on ligand distances and distortions from the regular tetrahedron.

More accurate measurements for manganese(II) chlorine and bromine have been performed by Mc Clure[7] and Pappalardo[8]. We must take care that only anhydrous materials are used for comparison, because only in these materials the Mn^{2+} ion is situated in octahedral sites with six identical Cl^- ligands (not exactly at the same distance from the central ion, however). Most reported studies are dealing with hydrated halides such as $MnCl_2 \cdot 2H_2O$ or $MnCl_2 \cdot 4H_2O$[7]. In the case of the crystal with $2\,H_2O$, the octahedron is made of 4 chlorine ions + 2 oxygen ions, in the case of the crystal with $4\,H_2O$ it is made of 2 chlorine ions + 4 oxygen ions. The shifts between anhydrous and hydrated materials are found to be about 1000 cm^{-1}, i. e. larger than the shifts observed by changing X = Cl into X = Br.

We shall remember here the positions of the main lines found previously[7-9]:

TABLE 4.

Compound		Absorption or excitation bands (cm^{-1}).				
		$^4T_1$ (^4G)	$^4T_2$ (^4G)	^4E (^4G)	$^4T_2$ (^4D)	^4E (^4D)
$MnCl_2$ anhydrous	4.2 K[7]	—	—	23.600	—	—
	78 K[8]	18.500	22.000	23.590 +23.825	26.750	28.065
$MnCl_2$, $2H_2O$	298 K[7]	18.980	21.050	24.130	26.800	28.650
	298 K[9]	19.030	21.440	24.320	26.840	28.740
$MnCl_2$, $4H_2O$	4 K[7]	18.740	22.600	24.475	27.230	29.090
	298 K[7]	18.870	22.730	24.600	27.470	29.070
$MnBr_2$ anhydrous	78 K[8]	18.450	21.650	23.084 +23.550	26.520	27.505
$MnBr_2$, $4H_2O$	4 K[7]	18.690	21.050	24.370	27.170	28.770

Manganese chloride and bromide, anhydrous or hydrated materials.

The above materials are very poorly luminescent. Now let us turn towards some complexes containing chlorine which show a red emission (octahedral coordination):

TABLE 5.

Compound	Emission	Excitation bands				
		$^4T_1(^4G)$	$^4T_2(^4G)$	$^4E(^4G)$	$^4T_2(^4D)$	$^4E(^4D)$
$C_5H_5NH)\,MnCl_3,\,H_2O$	15.300	18.350	21.460	23.800	26.670	28.170
$(CH_3)_4\,NMnCl_3$	16.450	18.540	22.490	23.750	27.030	28.170
$(C_2H_5NH_3)_2\,MnCl_4$	16.230	18.520	23.870	24.035	—	—

Position of the bands in cm^{-1}. All measurements at 4 K.

It is seen, the shift of the emission spectrum from one material to another extends over 1000 cm^{-1}. Pryidinium manganese(II) trichloride monohydrate as well as TMMC (tetramethylammonium manganese(II) trichloride) are well known to form antiferomagnetic linear chains[10], while ethylammonium tetrachloromanganate is often described as an example of *two-dimensional magnetic compounds*: this means that manganese ions are situated in parallel planes, while each manganese atom is embedded into a (strongly distorted) octahedron made by six chlorine ions[11].

In this class of compounds, most bromine complexes do not show a well-resolved structure and iodine compounds are highly unstable.

2.3. *The special case of antipyrin* + MnI_2. This material deserves a special study because of its interest in pharmacology. In addition, we found that its crystals are of remarkable stability. The preparation method was described in Ref. 12.

A broad emission band is observed (Fig. 2), whose peak position is almost the same as for pyridinium manganese(II) trichloride (not triiodide). But its width is even larger. An extremely wide absorption band has been observed in the visible, beginning near 360 nm and extending up to the infra-red, but no structure could be observed in this band (Table 6).

However it has been shown from crystallographic studies[12] and *EPR* measurements[13] that the ligands of the Mn^{2+} ion are in fact six oxygen ions belonging to the antipyrin groups, no bonding is observed between manganese and iodine (whence the peculiar stability of this material).

TABLE 6.

Compound	Temp.	Emission peak	Band-width (*)
Antipyrin + MnI_2	300 K	15.870	3.000
	4 K	15.270	2.400
$(C_5H_5NH)\,MnCl_3, H_2O$	300 K	15.300	2.450
$(C_5H_5NH)_2\,MnCl_4$	300 K	19.120	1.900

* Total width at half-maximum.
Emission characteristics (cm^{-1}).

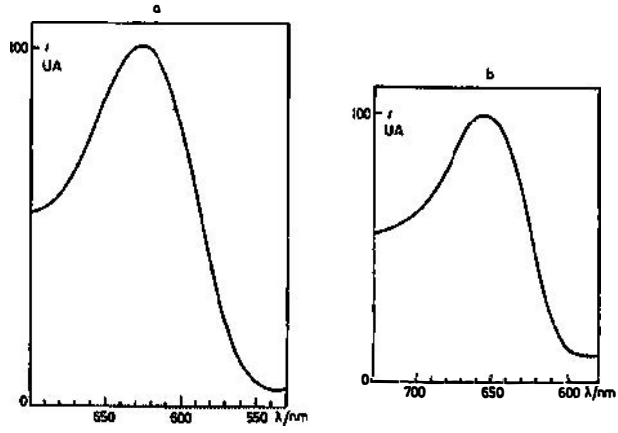

Fig. 2. The emission spectrum of the antipyrin + MnI_2 complex.
a) Room temperature; b) 4 K.

3. *Discussion*

An approximate idea on covalency is given by the reduction of Racah parameters B and C when the transition element is incorporated into the crystal: this effect has been referred to by Jørgensen as the *nephelauxetic* effect. The absorption/excitation bands $^6A_1\,(^6S) \rightarrow {}^4E\,(^4G)$ and $^6A_1\,(^6S) \rightarrow {}^4E\,(^4D)$ have been used for this computation, because:

1. these bands do not depend on the crystal field parameter Dq, and thus they allow us a direct calculation of the Racah parameters,

2. their position in most cases can be determined to a better accuracy than for any other band, such as the $^6A_1\,(^6S) \rightarrow {}^4T_1$ or $^4T_2\,(^4G)$.

As far as only electrostatic interactions are taken into account, the positions of the two levels $^4E(^4G)$ and $^4E(^4D)$ are given by the same expressions as for the corresponding free ion levels, that is:

$$^4E(^4G) \qquad 10\,B + 5\,C$$
$$^4E(^4D) \qquad 17\,B + 5\,C$$

From these expressions and the tables of experimental results reported above, we may derive the following numerical values:

TABLE 7.

Compound	$B/(\mathrm{cm}^{-1})$	$C/(\mathrm{cm}^{-1})$	C/B
Mn^{++} free ion	787	3795	4.82(*)
Tetrahedral coordination:			
$(C_5H_5NH)_2\,MnCl_4$ 4 K	653	3312	5.07
300 K	663	3314	5.00
$(C_5H_5NH)_2\,MnBr_4$ 4 K	643	3290	5.12
300 K	647	3324	5.14
$[(MePh_3)\,As]_2\,MnCl_4$ 4 K	665	3310	4.98
$[(MePh_3)\,As]_2\,MnBr_4$ 4 K	656	3265	4.98
$[(MePh_3)\,As]_2\,MnI_4$ 4 K	646	3153	4.88
Octahedral coordination:			
$MnCl_2$ anhydrous 78 K	639	3439	5.38
$MnCl_2, 2H_2O$ 298 K	631	3601	5.70
$MnCl_2, 4H_2O$ 4 K	659	3576	5.42
$MnBr_2$ anhydrous 78 K	632	3354	5.31
$MnBr_2, 4H_2O$ 4 K	629	3617	5.75
$(C_5H_5NH)\,MnCl_3, H_2O$ 4 K	624	3511	5.62
$(CH_3)_4\,NMnCl_3$ 4 K	631	3487	5.52

* Somewhat different values have been given by different authors, for instance see Ref. 14. Clearly a *best fit* computation between all observed levels will lead to different figures, introducing minor additional corrections too.

Electrostatic Racah parameters.

Now these calculations neglect the Racah-Trees correction $\alpha L\,(L+1)$ as well as the seniority correction $\beta\,Q$ (see for example Ref. 14 for the introduction of these correction into manganese ions). The seniority correction turns out not to be involved into ^4G and ^4D levels, hence we shall not take it into account. On the other hand, introducing the Racah-Trees correction increases the energies of all levels, which become now:

$$^4E(^4G) \qquad 10\,B + 5\,C + 20\alpha$$
$$^4E(^4D) \qquad 17\,B + 5\,C + 6\alpha$$

Let us denote by B' and C' the values of the Racah parameter which have been computed in Table 7, the *true* values will be given by:

$$10\,B + 5\,C + 20\alpha = 10\,B' + 5\,C'$$

$$17\,B + 5\,C + 6\alpha = 17\,B' + 5\,C'.$$

Hence

$$B' = B - 2\alpha \qquad C' = C + 8\alpha.$$

Therefore the high values of C'/B' which are observed on Table 7, especially for the case of octahedral coordination (but as a mater of fact this ratio is *always* found larger than for the free ion), can be ascribed indeed to an enhancement of the *Trees parameter* when the Mn^{2+} is incorporated into the material.

In Ref. 14, we computed $\alpha \sim 90\ cm^{-1}$ for $MnCl_2$ as well as in most octahedral compounds, instead of $\alpha = 65\ cm^{-1}$ for the free ion. But we were unable to compute any resonable set of parameters for the case of tetrahalomanganates. From Table 5 we see that will not be largely different from the free ion value for the case of triphenylmethylarsonium compounds, in which the ligand structure has been claimed to be an almost undistorted tetrahedron[5]. On the other hand, the distorsion in pyridine compounds has been extensively discussed in Ref. 15, using simultaneously cristallographical methods, *EPR* and optical effects of mechanical stresses.

Introducing instead of α the Koide and Pryce covalency parameter, on the contrary, will reduce the value of C'/B' below the free ion value (for the case of

TABLE 8.

Compound	$\Sigma E/\Delta E$
Mn^{++} free ion	10.74
Tetrahedral coordination:	
$(C_5H_5NH)_2\ MnCl_4$ 4 K	11.10
300 K	11.15
$(C_5H_5NH)_2\ MnBr_4$ 4 K	11.17
300 K	11.20
$[(MePh_3)\ As]_2\ MnCl_4$ 4 K	10.97
$[(MePh_3)\ As]_2\ MnBr_4$ 4 K	10.97
$[(MePh_3)\ As]_2\ MnI_4$ 4 K	10.83
Octahedral coordination:	
$MnCl_2$ anhydrous 78 K	11.54
$MnCl_2$, $2H_2O$ 298 K	12.00
$MnCl_2$, $4H_2O$ 4 K	11.60
$MnBr_2$ anhydrous 78 K	11.44
$MnBr_2$, $4H_2O$ 4 K	10.84
$(C_5H_5NH)\ MnCl_3$, H_2O 4 K	11.89
$(CH_3)_4\ NMnCl_3$ 4 K	11.75

a tetrahedral coordination) and therefore does not provide an explanation of the above effects[14].

Another parameter which has been found to be of interest is the ratio:

$$\frac{\Sigma E}{\Delta E} = \frac{{}^4E({}^4D) + {}^4E({}^4G)}{{}^4E({}^4D) - {}^4E({}^4G)}.$$

The study of this parameter leads to similar conclusion. (Table 8).

Here also, we observe values which are systematically larger than for the free ion, but the difference is particularly small for the case of triphenylmethylarsonium compounds. The difference between X = Cl and X = Br are exceedingly small, the difference between X = I and the two other halides involved in our complexes is larger.

We may conclude, the shift of levels ${}^4E({}^4G)$ and ${}^4E({}^4D)$ may give us by optical methods a characterization of the manganese ligands, which in most cases only supports the results previously known from *EPR* or crystallographical studies, but clearly optical methods are much simpler from the experimental point of view than the two other: they need a less sophisticated apparatus and they can be used easily when *EPR* or crystallographical results are not presently available.

On the other hand, the study of the Trees parameter α leads to conclusions on the nature of the coordination (tetrahedral or octahedral), and the degree of distortion from perfect cubic symmetry, rather than to conclusions on the nature, of the ligands. The study of the parameter $\Sigma E/\Delta E$ is not fundamentally different it looks rather as a more direct experimental way to derive the same results as from α.

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OPTIČKE KARAKTERISTIKE TETRAHALOMANGANATA I DRUGIH MANGANOVIH JEDINJENJA

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Originalni naučni rad

Pomeranje traka u emisionim spektrima manganovih(II) kompleksnih jedinjenja koja sadrže Cl, Br ili I su nešto malo veća od pomeranja u emisionim spektrima snimljenim na različitim temperaturama; međutim, ona su svakako manja od *slučajnih* pomeranja koja mogu na pr. poticati od različitog stepena hidratacije ispitivanog kompleksnog jedinjenja. Sa druge strane smanjenje veličine Racahovih parametara B i C, kao što se vidi iz apsorpcionih/ekscitacionih spektara, je u skladu sa očekivanjima na osnovu elementarnih razmatranja o kovalenci. Odnos C/B, kod Mn^{2+} jona ugrađenih u kompleksna jedinjenja, ukazuje da je povećan Treesov parametar α, čija veličina zavisi uglavnom od distorzije strukture liganda u tetraedru ili oktaedru.