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Chelate Complexes of Manganese(II): Synthesis, Spectroscopic and Electron Paramagnetic Resonance Properties of Manganese(II) β-Diketonate Derivatives

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The results of e.s.r., vibrational and electronic investigations were compared in order to describe the ligand field properties, the charge distribution and the nature of the chemical bonds in the adducts of bis-(2,4-pentanedionato)manganese(II) (Mn(pd)$_2$) with basic molecules.

E.s.r. data are suitable to describe axial and rhombic distortions caused by the additional base molecules. Phenanthroline, pyrazine and ethylenediamine give rise to axial distortion; dipyridyl, pyridine, 4-Mepyridine, quinoline, quinoxaline, water to rhombic distortion.

Both the steric hindrance and the electronic properties of the additional base ligand contribute to the distortion; however the electron-withdrawing power of the base decides the distortion weight. Intermolecular interaction in Mn(pd)$_2$ and in the adduct with pyrazine have also been considered by the e.s.r. data.

The manganese–pentanedionato bond properties and the bond strength internal to pentanedionato have been discussed by the i.r. data, in the light of the metal electronic structure and of the π acceptor properties of the additional base; the competition between pentanedionato and the additional base, as for the π acceptor power, is favourable to the pentanedionato ligand.

Introduction

The symmetry and bonding properties of chelate manganese(II) compounds cannot be easily considered by spectroscopic and spectromagnetic techniques. Indeed their electronic properties are not suitable for the ligand field investigation and the related infrared data are not sufficient to comment on the bonding properties; moreover the high spin d^5 configuration, spin only state ^{6}S, common to almost all these complexes, hinders the fine separation by means of their magnetic properties.

This paper reports an example of electron paramagnetic resonance investigation on some chelate manganese(II) compounds, that we had previously described by their magnetic behaviour [1].

The aim is to consider the stereochemistry and the charge distribution properties. The study has also been turned to investigating the nature and the mechanism of the metal–ligand–metal intermolecular interaction, frequent in complexes of this type [2] and in general to establishing that the properties of such a biologically interesting class of manganese(II) compounds can be in future more easily understandable.

Experimental

Preparation of Compounds

bis(2,4-pentanedionate)pyridinemetal(II): [M(pd)$_2$py] (M = Mn, Zn); bis(2,4-pentanedionate)bis(pyridine)manganese(II) [Mn(pd)$_2$(py)$_2$] bis(2,4-pentanedionate)bis(4-methylpyridine)manganese(II): [Mn(pd)$_2$(4-Mepy)$_2$]; bis(2,4-pentanedionate)(4-methylpyridine)zinc(II): [Zn(pd)$_2$(4-Mepy)].

These adducts were all prepared as follows: 10 mmol of [M(pd)$_2$(H$_2$O)$_2$] [3] (M = Mn, Zn) were dissolved in 50 ml of the base and were refluxed for 1 h. The solution was cooled at room temperature and the product precipitated by adding hexane.

The biadduct [Mn(pd)$_2$(py)$_2$] precipitated at 0 °C, while [Mn(pd)$_2$py] was obtained at room temperature. Elemental and thermal analyses are reported in Table I.

bis(2,4-pentanedionate)(4-methylpyridine)manganese(II): [Mn(pd)$_2$(4-Mepy)]; bis(2,4-pentanedionate)bis(quinoline)metal(II): [M(pd)$_2$(qui)$_2$] (M = Mn, Zn); bis(2,4-pentanedionate)pyrazinemetal(II): [M(pd)$_2$pz] (M = Mn, Zn); bis(2,4-pentanedionate)bis(quinoxaline)metal(II): [M(pd)$_2$(quinx)$_2$] (M = Mn, Zn); bis(2,4-pentanedionate)ethylenediaminemetal(II): [M(pd)$_2$en] (M = Mn, Zn); bis(2,4-pentanedionate)(α,α′-dipyridyl)metal(II): [M(pd)$_2$dipy] (M = Mn, Zn); bis(2,4-pentanedionate)(1,10-phenanthroline)metal(II): [M(pd)$_2$phen] (M = Mn, Zn).

These adducts were prepared as follows: 10 mmol (for monoadducts) or 20 mmol (for biadducts) of the base were added to a solution of 10 mmol of [M(pd)$_2$(H$_2$O)$_2$] (M = Mn, Zn) in 100 ml of hot ethanol and the resulting solution was refluxed for

TABLE I. Analytical, Thermal and Magnetic Susceptibility Data.[a]

Compound	M	C%		H%		N%		ΔT (°C)		L%	
[M(pd)$_2$py]	Mn	53.61	(54.22)	5.88	(5.72)	4.20	(4.22)	80–100		24.41	(23.79)
	Zn	52.75	(52.57)	5.28	(5.54)	4.16	(4.08)				
[M(pd)$_2$(py)$_2$]	Mn	58.15	(58.40)	5.90	(5.84)	6.70	(6.81)	20–45 1^st^L	80–100 2^nd^L	37.50	(38.53)
	Zn	58.15	(58.15)	5.90	(5.84)	6.70	(6.81)				
[M(pd)$_2$(4-Mepy)]	Mn	55.60	(55.50)	5.96	(6.05)	4.10	(4.05)	100–140		26.66	(27.45)
	Zn	53.04	(53.63)	5.80	(6.42)	3.90	(3.91)				
[Mn(pd)$_2$(4-Mepy)$_2$]		60.13	(60.14)	6.37	(6.38)	6.37	(6.38)	75–95 1^st^L	100–125 2^nd^L	41.21	(43.28)
[M(pd)$_2$(qui)$_2$]	Mn[b]							90–130		49.43	(50.48)
	Zn	65.65	(65.49)	5.33	(5.84)	5.45	(5.45)				
[M(pd)$_2$pz]	Mn[b]							100–140		24.50	(24.02)
	Zn	48.65	(48.69)	5.35	(5.79)	8.20	(8.11)				
[M(pd)$_2$(quinx)$_2$]	Mn[b]							110–160		50.01	(50.68)
	Zn	58.10	(59.42)	4.77	(5.33)	10.68	(10.66)				
[M(pd)$_2$en]	Mn	64.70	(64.10)	6.98	(7.06)	8.75	(8.90)				
	Zn	44.13	(44.30)	6.67	(7.30)	8.64	(8.61)				
[M(pd)$_2$dipy]	Mn	57.60	(58.60)	5.36	(5.37)	6.82	(6.85)				
	Zn	57.53	(58.39)	5.46	(5.83)	6.83	(6.81)				
[M(pd)$_2$phen]	Mn	59.60	(59.90)	3.97	(3.93)	6.36	(6.46)				
	Zn	58.37	(59.32)	5.16	(5.39)	6.23	(6.29)				

[a] L = pyridine (py), 4-Methylpyridine (4-Mepy), quinoline (qui), pyrazine (pz), quinoxaline (quinx), ethylenediamine (en), α,α'-dipyridyl (dipy), 1,10-phenanthroline (phen). L% = determined by thermal analysis. ΔT = temperature range of the loss of the ligand L, determined by thermal analysis. In brackets calculated values. [b] C%, H%, N% in ref. 1.

1 h. On cooling at room temperature, the adduct precipitated. It was filtered off and washed with ethanol. Analytical and thermogravimetric data are reported in Table I.

Preparation of the Doped Compounds

Diaquobis(2,4-pentanedionate)manganese(II) doped diaquobis(2,4-pentanedionate)zinc(II)–20%/80%

6.25 g of $MnCl_2$ (0.05 mol) and 27.00 g of $ZnCl_2$ (0.20 mol) were dissolved in 250 ml of water and 50 g of 2,4-pentanedione (0.5 mol) were added. The product precipitated by adding 68.1 g of CH_3COONa (0.5 mol dissolved in 150 ml of water) and 21 ml of aqueous 35% NH_3. It was filtered off and washed by cold water.

bis(2,4-pentanedionate)ligand (or bisligand)manganese(II) doped bis(2,4-pentanedionate)ligand (or bisligand) zinc(II) 80%/20%, 90%/10% (ligand = pyridine, 4-Mepyridine, pyrazine, quinoline, quinoxaline, α,α'-dipyridyl, ethylenediamine, 1,10-phenanthroline)

All these mixtures were prepared by the following general way: 2 mmol (or 4 mmol) of $[Mn(pd)_2(H_2O)_2]$ and 18 mmol (or 16 mmol) of $[Zn(pd)_2(H_2O)_2]$ were dissolved in hot ethanol, and 20 mmol (or 40 mmol) of the ligand were added. The mixture precipitated by cooling at room temperature. It was filtered off and washed by cold ethanol. The doped powders of the adducts with pyridine and quinoline had to be precipitated by adding n-hexane; they were filtered off and washed with n-hexane.

Apparatus

Vibrational spectra were recorded on a Perkin-Elmer 621 spectrophotometer, in KBr disc samples and electronic diffuse reflectance spectra on a Beckman DK-2A spectrophotometer. Magnetic susceptibility measurements were performed by the Gouy method; e.s.r. spectra were recorded on polycrystalline samples by a Varian E-4 spectrometer, and the g values evaluated by standardization with diphenylpicrylhydrazyl (DPPH). Thermal analyses have been carried out on a Dupont 900 apparatus equipped with a thermogravimetric analyzer Dupont 950 at a heating rate of 1 °C min^{-1} under a stream of nitrogen at 40 cm^3 min^{-1}.

Theoretical Treatment of E.s.r. Spectra

E.s.r. measurements of the Mn(II) complexes have been carried out on polycrystalline samples of the undiluted compounds and on Zn/mn mixed complexes (in ratios 90/10 or 80/20 depending on the sample). Only the spectra of diluted samples have been considered for the theoretical treatment and and for the evaluation of the magnetic parameters.

The dilution by zinc does not affect the magnetic field of manganese; however in the case of the adducts with pyridine, 4-Mepyridine and of anhydrous $Mn(pd)_2$ some differences in the magnetic field of the diluted samples with respect to the field of the undiluted ones will be considered.

The spectra were fit by an axial or rhombic spin Hamiltonian. For the axial compounds, in a high spin

TABLE II. X-Band Spectra of Mn(II) Complexes (undiluted polycrystalline samples).[a]

Compound	Field (G)
$[Mn(pd)_2phen]$	3360vs
$[Mn(pd)_2pz]$	3241vs
$[Mn(pd)_2en]$	3307vs
$[Mn(pd)_2(quinx)_2]$	1571m 2501vs 3011sh 3391sh 3771m 4431w 5151w
$[Mn(pd)_2(qui)_2]$	1770m 2570sh 3303s 3986vs 6103sh
$[Mn(pd)_2dipy]$	841w 2041s 3391vs
$[Mn(pd)_2(py)]$	1341w 2171sh 2711vs 3601sh 4191s 4981sh
$[Mn(pd)_2(py)_2]$	1024w 2391s 3491vs 4774sh
$[Mn(pd)_2(4\text{-}Mepy)]$	1251w 2141sh 2731vs 3521sh 4191m 4901w
$[Mn(pd)_2(4\text{-}Mepy)_2]$	1311w 2131sh 2641s 3441vs 4471sh
$[Mn(pd)_2(H_2O)_2]$	2015sh 3349vs
$[Mn(pd)_2]_3$	1732s 3399vs 4532m

[a]vs = very strong, s = strong, m = medium, sh = shoulder, w = weak. Recorded at room temperature.

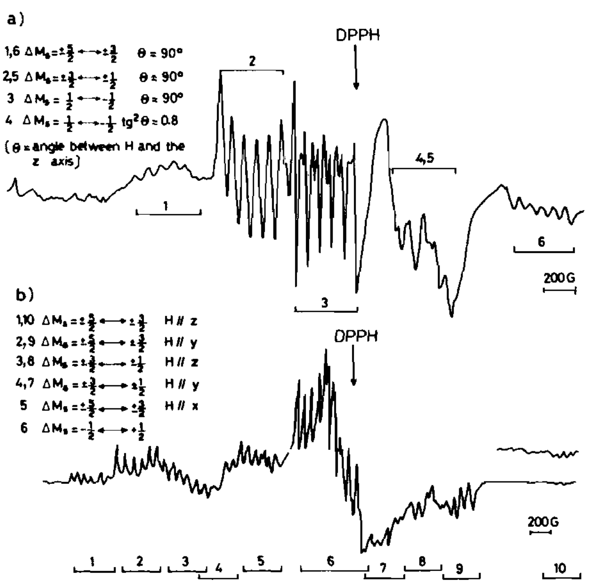

Fig. 1. X-Band E.s.r. spectra of diluted Zn/Mn powder of a) $[Zn/Mn(pd)_2pz]$ (80/20), b) $[Zn/Mn(pd)_2(qui)_2]$ (80/20) recorded at room temperature.

(S = 5/2) electronic configuration the representative spin Hamiltonian was that given by Bleaney and Ingram [4]:

$$\mathcal{H} = g\beta H + D[S_z^2 - 1/3S(S+1)] +$$
$$+ 1/6a[(S_\alpha^4 + S_\beta^4 + S_\gamma^4) - 1/5S(S+1)(3S^2 + 3S - 1)]$$
$$+ 1/180F[35S_z^4 - 30S(S+1)S_z^2 + 25S_z^2 - 6S(S+1) +$$
$$+ 3S^2(S+1)^2] + AS\cdot I$$

and the application to polycrystalline powders was that given by Woltermann and Wasson [5]. Among the three therms a, D and F, only D was considered for the contribution to the fine structure of the spectrum, due to the undetectable splitting in the powder spectra deriving from a and F interaction terms. The spectrum of $[Mn(pd)_2pz]$, in Zn/Mn 90/10 mixed powder, can be usefully considered as example (Fig. 1a). The fields of the resonances suggest axial symmetry and appreciable magnitude of the zero field parameter D. All the lines due to the zero field interaction split into six hyperfine resonances, due to the coupling with the nuclear spin of manganese.

The assignment of the lines of $Mn(pd)_2pz$ and of the other axial complexes is reported in Table III.

The D parameter has been evaluated by considering that the transitions $\Delta M_S = +5/2 \longleftrightarrow +3/2$ and $\Delta M_S = -5/2 \longleftrightarrow -3/2$ lie at field separated by 4D, the transitions $\Delta M_S = -3/2 \longleftrightarrow -1/2$ and $\Delta M_S = +3/2 \longleftrightarrow +1/2$ by 2D and the two transitions $\Delta M_S = +1/2 \longleftrightarrow -1/2$ ($\theta = 90°$; $tg\theta = 0.8$) by $5.6\ D^2/H_0$ (symbolism from ref. 5).

The results of the evaluation of $[Mn(pd)_2pz]$ spectrum and of the spectra of the other axial compounds are in Table IV.

For the compounds having rhombic symmetry the spin Hamiltonian is [5, 6]

$$\mathcal{H} = g\beta HS + D(S_z^2 - 1/3S(S+1) +$$
$$+ E(S_x^2 - S_y^2) + AS\cdot I$$

simplified for the zero field terms quadratic in spin.

The assignment of the lines in the spectrum of rhombic complexes is much more difficult than in the case of the axial complexes, due to higher number of lines of the zero-field interaction and mainly to their frequent overlap. However, starting from the spectrum of $[Mn(pd)_2(qui)_2]$ in Zn/Mn 80/20 mixed powder (Fig. 1b), the identification was attempted

TABLE III. X-Band Spectra of Mn(II) Doped Zn(II) Complexes.[a]

Compound	±5/2 ⟷ ±3/2 $\theta = 90°$	±3/2 ⟷ ±1/2 $\theta = 90°$	+1/2 ⟷ −1/2 $\theta = 90°$	+1/2 ⟷ −1/2 $tg^2\,\theta = 0.8$		
[Mn(pd)$_2$phen]	2210w, 4390w	2755sh, 3845sh	3045vs	3555vs		
[Mn(pd)$_2$pz]	2164w, 4556w	2762s, 3958s	3062s	3658s		
[Mn(pd)$_2$en]	1878w, 4822w	2614sh, 4086sh	2895s	3805s		
	±5/2 ⟷ ±3/2 H∥z	±5/2 ⟷ ±3/2 H∥z	±3/2 ⟷ ±1/2 H∥z	±3/2 ⟷ ±1/2 H∥y	±5/2 ⟷ ±3/2 H∥x	+1/2 ⟷ −1/2
[Mn(pd)$_2$(quinx)$_2$]	791m	1841m	2111w	2571ms, 3891ms	2831w	3360vs
[Mn(pd)$_2$(qui)$_2$]	711w, 5731w	1231ms, 4111ms	1991m	2451ms, 3851ms	2461ms	3290vs
[Mn(pd)$_2$dipy]	1211w, 5340w	1321w	1571vw	2641m, 4341m	3091ms	3791vs
[Mn(pd)$_2$(py)$_2$]	1581w, 4221w			2521ms, 3751ms		3421vs
[Mn(pd)$_2$(4-Mepy)$_2$]	1531w, 4531w		2711m, 4201m	2791ms, 3961ms		3391vs
[Mn(pd)$_2$(H$_2$O)$_2$]			2100ms, 4900ms	2933m, 4066m		3483vs

[a] Field of resonances in Gauss.

TABLE IV. E.s.r. Parameters of Mn(II) Complexes.

Compound	D(G)	E(G)	E/D[a]	A(G)
[Mn(pd)$_2$phen]	545	0	0	unresolved
[Mn(pd)$_2$pz]	598	0	0	80
[Mn(pd)$_2$en]	736	0	0	80
[Mn(pd)$_2$(quinx)$_2$]	660	<30	<<0.33	80
[Mn(pd)$_2$(qui)$_2$]	627	<30	<<0.33	75
[Mn(pd)$_2$dipy]	516	110	0.21	85
[Mn(pd)$_2$(py)$_2$]	330	95	0.29	70
[Mn(pd)$_2$(4-Mepy)$_2$]	375	68	0.18	80
[Mn(pd)$_2$(H$_2$O)$_2$]	700	<<30	<<0.33	80

[a] E/D is indicative of the number of transitions belonging to the $\Delta M_S = +1/2 \longleftrightarrow -1/2$ and of their field separation.

for all the rhombic compounds here reported, by the method of Woltermann and Wasson. The best possible assignment of the lines for the rhombic compounds is in Table III. The magnetic parameter values are in Table IV, where, for the rhombic complexes, the value of the E/D ratio gives an idea of the spectrum complexity in the field region assigned to the components of the $\Delta M_S = +1/2 \longleftrightarrow -1/2$ transition.

The *g* values of all complexes reported in this paper are indistinguishable from the free electron value, within the limits of the *g* standardization.

It must finally be observed that not all the complexes show well resolved spectra like those reported as examples; however, the evaluation of the magnetic parameters was possible in all cases, also supported by the preliminary indications from the spectra of the undiluted compounds and by the large number of examined complexes.

Results

E.s.r. Investigation

All the Mn(II) complexes have high spin electronic configuration, with five unpaired electrons in the ground state. The magnetic susceptibility measurements of some of them have been consiered in a previous paper [1].

E.s.r. investigation on all the Mn(II) compounds here reported has been carried out both on pure polycrystalline powders and on Mn(II)/Zn(II) doped polycrystalline powders. Spectromagnetic results have been compared within the series of the Zn doped powders, to prevent the interference of the different diamagnetic matrix.

Undiluted powders exhibit spectra, at room temperature, with features characteristic of $S = 5/2$ d^5 metal ions. The resonance fields of the e.s.r. transitions of the spectra of the undiluted powders, reported in Table II, divides the Mn(II) complexes in

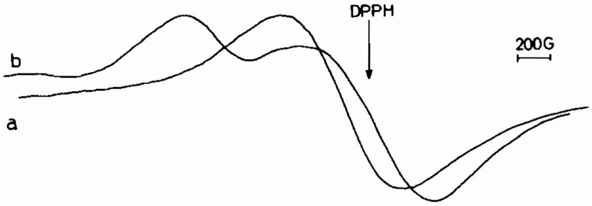

Fig. 2. X-Band E.s.r. spectra of a) $[Mn(pd)_2(pz)]$, b) $[Mn(pd)_2(dipy)]$ recorded at room temperature in polycrystalline undiluted samples.

two series with different symmetry [7]: $[Mn(pd)_2phen]$, $[Mn(pd)_2pz]$, $[Mn(pd)_2en]$, having higher symmetry; $[Mn(pd)_2(H_2O)_2]$, $[Mn(pd)_2]$, $[Mn(pd)_2py]$, $[Mn(pd)_2(py)_2]$, $[Mn(pd)_2(4\text{-}Mepy)]$, $[Mn(pd)_2(4\text{-}Mepy)_2]$, $[Mn(pd)_2(qui)_2]$, $[Mn(pd)_2(quinx)_2]$, $[Mn(pd)_2(\alpha,\alpha'\text{-}dipy)]$ having lower symmetry. The shapes of the spectra make this difference evident (Fig. 2).

An e.s.r. investigation more useful for describing the field properties can be carried out by Zn/Mn diluted powders. The availability of these analyses strongly depends on the dilution of the complexes; and not all the compounds proved equally suitable for the mixture. The most representative diluted powders, as for the calculation of the zero-field terms, are that of the pyrazine derivative (axial symmetry) and of the quinoline derivative (rhombic symmetry) (Fig. 1); however, the analysis of the e.s.r. spectra of the diluted powders gives a measure of the axial and of the rhombic distortion for all the Mn(II) compounds here reported. The three axial compounds $[Mn(Pd)_2(phen)]$, $[Mn(pd)_2pz]$, $[Mn(pd)_2en]$, have all large values of the zero field parameter D; the g values show no detectable differences from the free electron value and the A values are indicative of considerable bond covalency (Table IV). The most interesting feature is that pyrazine, for which a *trans* axial bicoordination with respect to the plane of the pentanedionates has been suggested [1], causes distortions similar to those of chelating phenanthroline and ethylenediamine (within an error of about ±15% in the D values).

As for all the other $Mn(pd)_2$ derivatives, they show rhombic distortions that clearly separate the adducts with dipyridyl, pyridine and 4-Mepyridine from those with quinoline, quinoxaline and water. The g and A values are comparable with those of the axial compounds.

The trend of distortion of all pd derivatives cannot be related to the geometric properties of the groups bonding Mn(II) or to their electronic properties, separately. Both contribute in deciding the symmetry of the ligand field. Really, on the basis of the steric hindrance of the ligands in the axial position, the adduct with pyrazine should not reveal large differences in its distortion with respect to the adducts with pyridine and 4-Mepyridine. The higher symmetry of $[Mn(pd)_2pz]$ with respect to $[Mn(pd)_2py]$ and $[Mn(pd)_24Mepy]$ can be explained by electronic differences in the π acceptor properties of the pyrazine with respect to the other two base molecules. It is reasonable to suppose that if the ligands in axial position have an electron π affinity similar to that of the equatorial pentanedionates, the electronic distribution on the whole molecule as well as the magnetic properties can have higher symmetry. In the case of the pyrazine derivative, the magnetic susceptibility measurements showed that the electrons are exchanged between two manganese centers, through the pyrazine ring; this effect increases the ability of pyrazine to accept π electrons from manganese. The magnetic exchange coupling can be extended to the Zn/Mn mixed powders. Really the analogy between the symmetry deducible from the e.s.r. spectra of the undiluted $[Mn(pd)_2pz]$ and of its Zn/Mn mixed powder suggests that the interposed zinc–pyrazine system does not have influence on the magnetic behavior of the manganese compound; and it is probable that the magnetic exchange, revealed by the undiluted powder, goes uninterrupted from a Mn center to another through a Mn–pyrazine–Zn–pyrazine–Mn chain. The equivalence between the shape of the e.s.r. spectra of the diluted and the undiluted pyrazine adducts also confirms the polymeric structure of the Mn compound, already proposed. Indeed, if it had dimeric, trimeric or a structure with a limited number of interacting metal centers, the resulting e.s.r. spectrum of the undiluted compound should be dramatically different from that of the mixed powder, without equivalence of the manganese centers.

On the basis of the steric properties the adduct with phenanthroline should have higher distortion than the adduct with dipyridyl; however the possibility of interaction between the π system of α,α'dipyridyl and that of manganese is certainly smaller than in the case of phenanthroline, so that the higher rhombic distortion power of α,α'-dipyridyl can be explained.

The comparison between the α,α'-dipyridyl and o-phenanthroline shows that the weight of the electron π acceptor properties overcomes that of steric hindrance and that the effect of electron-withdrawing power opposes the steric effect as for the rhombic distortion of the complexes.

Pyridine and 4Me-pyridine adducts derive their position in the rhombic distortion trend with respect to quinoline and quinoxaline adducts from the lower π acceptor power of the base, despite the lower steric hindrance of the single benzene ring. So the electron-withdrawing effect is more important than the steric hindrance for determining the trend of the rhombic distortion.

The monoadducts with pyridine and 4-Mepyridine become biadducts by dilution with the Zinc complexes.

Low rhombic distortions have been found in $[Mn(pd)_2(H_2O)_2]$ and $Mn(pd)_2$. It must be observed that diluted $Mn(pd)_2$ shows lower distortion than expected from the undiluted powder spectrum. This suggests that dilution changes the symmetry of the ligand field around manganese, like in the case of pyridine and 4-Mepyridine.

If one consider that $Mn(pd)_2$ has a trimeric structure [9], confirmed by the magnetic susceptibility measurements [10], it seems probable that the symmetry of this structure can be dramatically changed by substitution of Mn by Zn.

Lower or no changes are expected in case of polymeric structure [1], as observed for $[Mn(pd)_2pz]$ compound.

In conclusion, all the manganese compounds discussed here show the rhombic distortion clearly related to the π acceptor effects of the additional base molecule, while the tetragonal distortion is more depending on the combined effects of steric hindrance and of electron-withdrawing power of the molecule. Perhaps the E/D ratio gives an idea of the whole distortion.

Electronic and Vibrational Investigation

Electronic investigation, performed on powder samples by diffuse reflectance techniques, gives poorly differentiating spectra of the Mn(II) complexes. Indeed the d–d electronic transitions, usually characterizing the ligand field, are all spin forbidden in the high spin d^5 configuration and have very low intensity. Table V reports the frequencies of the most probable d–d absorptions. More detailed assignment is nonsense, because there is no difference from one compound to another.

Vibrational spectra, in the range 1800–200 cm^{-1}, show the bands characteristic of the ligands in the field of the examined ions; and the spectral dependence on the metal was studied by comparison among the spectra of Mn and Zn complexes. Results are in Table VI where only the absorptions due to $\nu(C\cdots O)$, $\nu(C\cdots C)$ and $\nu(M–O)$ have been assigned. The assignment is in agreement with that reported for analogous complexes [11].

The vibrations due to M–O stretching mode show a single band in all the reported compounds, with the exception of $Mn(pd)_2$ and $Mn(pd)_2(\alpha,\alpha'$-dipyridyl). So the perturbation of the ligand field symmetry, surely proved by the e.s.r. analysis, is much less visible by the i.r. spectra and the apparent symmetry of a large number of compounds is higher than the real. The additional ligands do not perturb the metal field enough to separate the vibrational M–O stretching frequencies, as expected in case of rhombic distortion. Only the trimerization of $Mn(pd)_2$ and the coordination of α,α'-dipyridyl split these vibrations in three and two components respectively.

The singular behavior of the vibrational properties of $Mn(pd)_2$ is in agreement with the distortion visible from the e.s.r. spectrum of this undiluted compound; in a similar way the large rhombic distortion shown by the e.s.r. spectrum of $Mn(pd)_2(\alpha,\alpha'$-dipyridyl) is confirmed. The different frequencies of the $\nu(M–O)$ (M = Mn, Zn) are indicative of the related different energies and their values suggest that the M–O bond strength depends on the occupation of both d_π and d_σ orbitals. The frequencies of the bands $\nu_{as}(C\cdots O)$, $\nu_{as}(C\cdots C)$, $\nu_s(C\cdots O)$, $\nu_s(C\cdots C)$ help in discussing the distribution charge in the molecules of our complexes. Though the differences are very thin, they suggest that:

i) the asymmetric stretching $\nu_{as}(C\cdots O)$ is the most sensitive vibration to addition of a basic group, like pyridine, pyrazine, ethylenediamine *etc.*

ii) the addition of a basic ligand having π acceptor properties lowers the frequency median of those related to the pentanedionate π system (which can be assumed as representative of the π bond strength internal to the pd system). So it can be assumed that the π acceptor properties of the additional ligand do not successfully compete with the π acceptor properties of pd; the back donation in plane (see vibrational frequencies of pyridine, 4-Mepyridine, quinoline, quinoxaline adducts) increases by addition of the basic molecules, very probably due to increased σ electron density on manganese and gives, as a consequence, higher occupation of the π^* system of pd. If the coordination of the base removes the planarity of pd group (see the adducts with chelating ligands) the decrease in frequency is not observed, as expected; moreover less basic groups, like water or pentanedionate (in $[Mn(pd)_2(H_2O)_2]$ and $Mn(pd)_2$), do not increase the π back donation.

TABLE V. Diffuse Reflectance Electronic Data of $Mn(pd)_2$-$L_{1,2}$ Derivatives.[a]

Compound	ν_1 (cm^{-1})	ν_2 (cm^{-1})
$[Mn(pd)_2]_3$	8.700(m)	20.000(sh)
$[Mn(pd)_2(H_2O)_2]$	not visible	not visible
$[Mn(pd)_2pz]$	12.500(vw)	not visible
$[Mn(pd)_2phen]$	15.000(vw)	21.000(sh)
$[Mn(pd)_2en]$	12.500(vw)	20.000(sh)
$[Mn(pd)_2dipy]$	12.500(vw)	16.000(sh)
$[Mn(pd)_2(py)_2]$	12.500(vw)	20.000(sh)
$[Mn(pd)_2(4\text{-}Mepy)_2]$	12.500(vw)	not visible
$[Mn(pd)_2(qui)_2]$	12.500(vw)	21.500(sh)
$[Mn(pd)_2(quinx)_2]$	not visible	not visible

[a] vw = very weak, sh = shoulder, m = medium.

TABLE VI. Vibrational Data (cm^{-1}).

Compound	M	ν_{as}(C⋯O) ν_{as}(C⋯C)	ν_s(C⋯O)	ν_s(C⋯C)	ν(M–O)	Other Bands							
[M(pd)$_2$]	Mn	1605	1465	1260	450, 425, 400	1515	1405	1195	1018	922	800, 770	660, 650	540
[M(pd)$_2$(H$_2$O)$_2$]	Mn	1605	1465	1260	412	1525	1400	1202	1020	928	770	670, 660	550
	Zn	1595	1445	1260	410	1510	1395	1190	1018	930	770	650	550
[M(pd)$_2$py]	Mn	1595	1445	1250	400	1510	1400	1190	1010	918	760	650	540
	Zn	1590	1450	1260	410	1518	1400	1190	1012	922	770	650	550
[M(pd)$_2$(4-Mepy)]	Mn	1615, 1605	1460	1255, 1242	410	1520	1400	1195	1020	923	775	655	548, 542
	Zn	1590	1460	1260	420	1520	1405	1198	1018	928	772	625	555
[M(pd)$_2$(4-Mepy)$_2$]	Mn	1590	1460	1260	400	1515	1410	1195	1015	920	765	660, 650	540
[M(pd)$_2$(qui)$_2$]	Mn	1580	1455	1250	400	1518	1400	1190	1010	920	765	650	540
	Zn	1590	1465	1260	418	1512	1398	1192	1010	925	765	650	551
[M(pd$_2$pz]	Mn	1610	1455, 1430	1250	420, 400	1510	1390, 1370	1190	1010	915	760	650	538
	Zn	1600	1450	1252	408	1505	1387	1188	1012	915	760	650	550
[M(pd)$_2$(quinx)$_2$]	Mn	1592	1455	1258	402	1518	1405	1208	1010	920	758	652	542
	Zn	1590	1453	1260	405	1518	1410	1208	1015	925	778	653	552
[M(pd)$_2$en]	Mn	1615	1450	1248	400	1508	1400	1190	1010	920	768	652	532
	Zn	1618	1455	1250	409	1510	1405	1195	1018	915	770	655	540
[M(pd)$_2$dipy]	Mn	1610, 1590	1465	1260	415, 400	1525	1420	1200	1020	925	780	650	540
	Zn	1595	1460	1250	410	1510	1400	1190	1010	918	770	648	542
[M(pd)$_2$phen]	Mn	1590	1455	1250	405	1510	1400	1190	1020	918	760	660	540
	Zn	1592	1450	1252	405	1510	1400	1192	1015	920	765	650	545

A peculiar case is shown by the pyrazine adduct, where the coordination of a basic molecule in axial position increases the median pd frequencies; it can be suggested that the electron exchange among the unities of this polymeric system, *via* π system of pyrazine, successfully competes with the π system of pd for the acception from manganese.

iii) The weight of the π back donation in the manganese compounds is also confirmed by an analogous trend of frequencies observed in the zinc compounds. The effects of the basic additional ligand are enhanced by the higher back donating power of zinc with respect to manganese.

Conclusions

Three main points of conclusion can be drawn from the reported results:

i) The addition of one or two ligands to the parent [Mn(pd)$_2$] compound changes the symmetry of the ligand field, depending on both steric and electronic properties of the additional molecule. The effect of the electronic properties mainly of the electron-withdrawing power, successfully competes with the steric hindrance effect.

ii) The results of the e.s.r. investigation measurements confirm the hypothesis of magnetic exchange formulated by the magnetic susceptibility measurements.

As for the mechanism of the magnetic exchange, the Anderson [12] theory can be invoked. [Mn(pd)$_2$]$_3$, to which a trimeric molecular structure can be assigned, shows antiferromagnetic behavior and this effect may be considered as resulting from two component effects, due to its d^5 high spin electronic ground configuration: a) interaction between the central metal ion and the two terminal ions is related to superexchange magnetic interaction involving two half filled d metal orbitals (for example $d_{x^2-y^2}$ and d_{xy}) having such symmetry that the metal orbitals can be expanded by the ligand orbitals of available symmetry (2p oxygen orbitals). The effect of this interaction is antiferromagnetic.

Moreover the same magnetic interaction is related to 'true direct exchange', as there are half filled orthogonal orbitals on every Mn center. The result of this interaction is the ferromagnetic effect. b) Interaction between the two terminal ions is related to superexchange magnetic interaction involving two d metal orbitals having symmetry available to be expanded by the π system of pentanedionate anion (d_{xy} or $d_{x^2-y^2}$). The result is antiferromagnetic. The resulting effect of a) and b) is an antiferromagnetic behavior of Mn(pd)$_2$, as experimentally found.

In the case of Mn(pd)$_2$pyrazine compound the only way of interaction possible with the hypothesized *trans* coordination of two pyrazine molecules, each common to two Mn ions, is a magnetic superexchange interation between two half filled Mn d orbitals, having symmetry available to be expanded by the π system of pyrazine (d_{xy} or d_{yz}). The effect is antiferromagnetic and, due to the loss of any ferromagnetic contribution, the strength of the exchange is higher in Mn(pd)$_2$pyrazine, than in [Mn(pd)$_2$]$_3$.

iii) In all the reported compounds back donation is possible between the metal and the pentanedionate anions and the metal and the additional ligand. The effects of back donation determine the strength of the Mn–O bond. The competition between the back donation to pd and to the additional ligand is favourable to pd, mainly in complexes having the two pentanedionates in the sampe plane, because they have the π^* orbital system more apt to accept charge from the metal, specifically more apt to be affected by the variation of charge on the metal by the additional basic ligand.

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