The Coordination Chemistry of Phosphoryl Compounds Containing the $-N(CH_3)_2$ Group, XIII¹
**ESR Spectra of Some Manganese(II) Complexes
of Hexamethylphosphoramide and Nonamethylimidodiphosphoramide**

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Room temperature electron spin resonance powder spectra have been recorded for some compounds of the type $Mn(\text{ligand})_p(\text{anion})_2$ with hexamethylphosphoramide and nonamethylimidodiphosphoramide as ligands ($p = 1-4$) and BF_4^- , NO_3^- , Cl^- , Br^- , I^- and NCS^- as anions.

The values for the zero-field parameters, D and λ , have been determined and are compared with literature data. It is shown that ESR spectroscopy can be very helpful in elucidating the structures of manganese(II) complexes.

The high values for the hyperfine coupling constant of the solvates suggest that in these complexes the bonding between the ligands and the metal ion is essentially ionic.

In some recent papers²⁻⁶ we described the donor properties of the ligands hexamethylphosphoramide (HMPA) and nonamethylimidodiphosphoramide (NIPA). It was shown that the oxygen atoms of the ligands act as the donor atoms in metal complexes of these ligands.

The physical measurements applied to the Mn(II) complexes of these ligands (ligand-field spectroscopy, IR spectroscopy and X-ray powder diffraction) did not yield conclusive information about the bonding in and geometry of these complexes⁶; tentative assignments however could be made. Therefore it seemed interesting to study the ESR spectra of some manganese(II) complexes, in order to obtain more detailed information about the bonding and geometry. Furthermore, it was hoped that the ESR parameters (the zero-field parameters D and λ , and the hyperfine coupling constant A) could be correlated with results obtained from the other physical measurements.

The present paper therefore describes the ESR spectra for a number of manganese(II) complexes of HMPA and NIPA.

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Experimental

All complexes were prepared as described previously^{2, 3, 6}. Paramagnetic resonance spectra at X- and Q-band frequencies were recorded on Varian instruments by methods described elsewhere⁷ (with the assistance of Mr. P. G. VAN DEN AKKER). The calculations were carried out on the IBM 360/65 computer at Leyden University, with a Fortran IV program written by R. D. DOWSING⁷ and modified by one of the authors.

Results and Discussion

The results of the calculations on the present compounds are listed in Table I. Figs. 1–3 show some representative spectra illustrating band widths, band shapes and fine structure.

ESR spectra of Mn(II) compounds can be used to differentiate between distorted octahedral and tetrahedral complexes. Complexes of D_{4h} symmetry, for instance, yield values of λ close to zero, while complexes of C_{2v} (pseudotetrahedral) symmetry yield values of λ close to $1/3$ ⁸. In most cases it is therefore quite easy to deduce the most probable local symmetry from the ESR spectral data. Only when D is

Tab. I. Zero-field parameters for some pure and diluted manganese (II) complexes of HMPA and NIPA*.

Compound	D^{**} (cm^{-1})	λ^{**} ($=E/D$)	A^{**} (10^{-4}cm^{-1})	Structure and most probable local symmetry
$\text{Mn}(\text{HMPA})_2\text{I}_2$	0.62(1)	0.20(2)	—	pseudo-tetrahedral, C_{2v}
$\text{Zn}(\text{Mn})(\text{HMPA})_2\text{I}_2$	0.62(1)	0.20(2)	74(2)	idem****
$\text{Mn}(\text{HMPA})_2\text{Br}_2$	0.42(1)	0.25(2)	—	idem
$\text{Mn}(\text{HMPA})_2\text{Cl}_2$	0.31(1)	0.23(2)	—	idem
$\text{Mn}(\text{HMPA})_2(\text{NCS})_2$	0.03(1)	—	—	idem***
$\text{Zn}(\text{Mn})(\text{HMPA})_2(\text{NCS})_2$	0.034(2)	0.29(1)	80(2)	idem***
$\text{Zn}(\text{Mn})(\text{HMPA})_2(\text{NO}_3)_2$	0.027(3)	$\sim 0.0(1)$	86(3)	pseudo-octahedral, D_{2h} ***
$\text{Cd}(\text{Mn})(\text{HMPA})_4(\text{BF}_4)_2$	≤ 0.001	—	84(3)	tetrahedral, T_d
$\text{Mn}(\text{NIPA})_2\text{I}_2$	0.70(2)	0.025(5)	—	pseudo-octahedral, D_{2h} ****
$\text{Mn}(\text{NIPA})\text{Br}_2$	0.44(1)	0.20(2)	—	pseudo-tetrahedral, C_{2v} ****
$\text{Mn}(\text{NIPA})\text{Cl}_2$	0.41(1)	0.21(2)	—	idem
$\text{Mn}(\text{NIPA})(\text{NCS})_2$	0.02(1)	—	—	idem***
$\text{Mn}(\text{NIPA})(\text{NO}_3)_2$	0.075(5)	0.033(6)	—	pseudo-octahedral, D_3 ***
$\text{Zn}(\text{Mn})(\text{NIPA})_3(\text{BF}_4)_2$	0.010(5)	—	90(3)	idem***

*: All complexes have g -values of 2.00.

**: Uncertainties in the last digit are in parentheses.

***: These assignments were reached by combination of the ESR measurements with measurements described earlier (see text).

****: The spectra showed an impurity with octahedral symmetry to be present.

Fig. 1. X-band spectrum of $\text{Mn}(\text{NIPA})(\text{NO}_3)_2$. Fig. 3. Q-band spectrum of $\text{Mn}(\text{HMPA})_2\text{Cl}_2$. Fig. 2. Q-band spectrum of $\text{Mn}(\text{NIPA})_2\text{I}_2$.

very small, problems occur. In these cases additional information (*i.e.* measurements on Mn(II)-doped diamagnetic compounds, ligand-field or IR spectral data, X-ray isomorphy) is necessary to make a definite structure assignment.

As can be seen from Table I, this problem occurs with some of our complexes (marked *** in Table I). However, combination of the ESR measurements with measurements described earlier^{2, 3, 6}, led to the assignments presented in Table I. In all other cases the structure assignments followed directly from the ESR spectral data. A comparison with results from other physical measurements^{2, 3, 6} does not show discrepancies: All previous (tentative) assignments are confirmed.

An interesting aspect is the presence of octahedral impurities in tetrahedral complexes (or, more general,

the presence of Mn(II) in different environments)⁸. This was also observed by GOODGAME *et al.*⁹ for the compound $\text{Mn}(\text{Ph}_3\text{AsO})_4\text{I}_2$. In the case of the NIPA complexes, we believe the impurity to be $\text{Mn}(\text{NIPA})_3^{2+}$, since this moiety is known to be unexpectedly stable^{3, 4, 6}. In the case of the HMPA compound, the exact nature of the impurity cannot be specified.

Of interest are the values for the hyperfine coupling constants of the solvates. As listed in Table I, the value of A for the octahedral (NIPA) solvate is larger than that for the tetrahedral (HMPA) solvate. Using TITLE's¹⁰ correlation between the magnitude of A and the PAULING ionicity of the lattice, this means decreased ionicity in the tetrahedral case^{10, 11}. This not only agrees with observations on MnCl_6^{4-} and MnCl_4^{2-12} , but also parallels the results from the ligand-field spectral and MÖSSBAUER measurements on HMPA and NIPA complexes^{2, 3, 5, 6}. Comparing the observed A values with that reported for $\text{MnF}_6^{4-}(91 \cdot 10^{-4} \text{ cm}^{-1})^{13}$, it shows that the manganese (II)-ligand bonding in the phosphoryl solvates is essentially electrovalent. This conclusion was drawn earlier for complexes of other divalent metal ions and this class of ligands^{2-6, 14, 15}. With respect to the values of the zero-field parameters for the various complexes, the following remarks can be made: For the pseudo-tetrahedral complexes, the anion sequence with respect to increasing D values is $\text{NCS}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$. This sequence goes parallel with the spectrochemical series for these anions². The same order was found by DOWSING *et al.*⁸ for some pseudo-tetrahedral triphenylphosphine and arsine oxide complexes. It was remarked by these authors that this order corresponds to that of the size of the donor atoms; anyway, the sequence is as expected for a distortion parameter.

The very small D value for Mn^{2+} in $\text{Cd}(\text{HMPA})_4(\text{BF}_4)_2$ is in accordance with a regular tetrahedral structure for this compound. The small D and λ values for the pseudo-octahedral nitrate complexes can be explained in terms of an all-oxygen environment of the metal ions; the same holds for the tris-NIPA complex. This means that the NO_3^- ions must act as bidentate ligands in the HMPA and NIPA complexes. The rather large D value and the small λ value for the compound $\text{Mn}(\text{NIPA})_2\text{I}_2$ are in accordance with a trans-octahedral molecular unit⁷.

The low D values of the pseudo-tetrahedral thiocyanato complexes (which made it impossible to determine the λ values) are very interesting. DOWSING

*et al.*⁸ obtained a similar result for the compound $\text{Mn}(\text{Ph}_3\text{AsO})_2(\text{NCS})_2$ ($D = 0.045 \text{ cm}^{-1}$), although a λ value of 1/3 was assumed for this compound. The explanation for this behaviour is not clear; it is quite possible that this is connected with the fact that the NCS^- ion occurs at a higher position in the spectrochemical series than the phosphoryl ligands, while the halogen ions occur at lower positions^{2, 6}.

Conclusion

Regarding the results discussed above, the following conclusions can be drawn:

1. ESR spectra of Mn(II) complexes can be used to differentiate between distorted octahedral and tetrahedral complexes; only when D is very small, direct assignments are not possible.
2. For pseudo-tetrahedral complexes the distortion parameters agree with the spectrochemical positions of the anions.
3. Particularly in the octahedral solvates, the bonding between the Mn(II) ions and the phosphoryl ligands is predominantly electrovalent.

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