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The Coordination Chemistry of Manganese(II). Part 13 [1]. The Synthesis of Manganese(II) Selenocyanate and its Complexes with Oxygen, Sulphur, Nitrogen and Phosphorus Donor Atoms

C. G. BENSON, M. G. LITTLE

Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD, U.K.

and C. A. McAULIFFE*⁺

Department of Chemistry, Auburn University, Auburn, Ala. 36849, U.S.A.

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Manganese(II) selenocyanate has been successfully prepared from manganese(II) chloride and potassium selenocyanate under strictly anhydrous conditions. The infrared and electron spin resonance spectra of manganese(II) selenocyanate differ significantly from those of the analogous manganese(II) thiocyanate salt. Several 1:1 Mn(ligand)(NCSe)$_2$ (ligand = EtOH, PPh$_3$, PPhMe$_2$), 1:2 Mn(ligand)$_2$(NCSe)$_2$ (ligand = tetrahydrofuran, THF), and 1:4 Mn(ligand)$_4$(NCSe)$_2$ (ligand = OPPh$_3$) complexes have been prepared and characterised by spectroscopic and magnetic measurements. The monomeric Mn(THF)$_3$(NCSe)$_2$ appears to have a trans *trigonal bipyramidal structure, as predicted by Norbury. The Mn(ligand)(NCSe)$_2$ (L = PPh$_3$, PPhMe$_2$) complexes show no tendency to coordinate dioxygen.*

Introduction

Although manganese(II) forms an extensive series of salts with all common anions [2], manganese(II) selenocyanate, Mn(NCSe)$_2$, has never been isolated. There are several reports of *in situ* preparations [3–5] including ionic species such as $Mn(NCSe)_n^{(n-2)-}$ in solution (n = 1–6) [3] and as solids (n = 4, 6) [4, 5]. Although there is a report of Mn(NCSe)$_2$(dioxan) [3], very few complexes Mn(NCSe)$_2$L$_n$ have been reported.

Our interest in the reversible dioxygen carriers MnX$_2$(PR$_3$) [6] (X = Cl, Br, I, NCS) has led us to attempt to isolate manganese(II) phosphine complexes containing the selenocyanate anion, especially in view of the fact that we observe some very interesting structure/reactivity relationships towards dioxygen binding in the Mn(NCS)$_2$(PR$_3$) series of complexes [6].

We have thus synthesized and characterized anhydrous manganese(II) selenocyanate, and although we have successfully isolated Mn(NCSe)$_2$(PR$_3$) and Mn(NCSe)$_2$(PPhMe$_2$), neither show any ability to bind dioxygen. We report here these complexes and have further extended the co-ordination chemistry of this rare manganese(II) salt.

Results and Discussion

The compounds isolated are listed in Table I and the preparative reactions are outlined in the Scheme.

Manganese(II) selenocyanate has not been hitherto isolated although it has previously been prepared *in situ* [3]. In previous attempts [3] few precautions have been taken to maintain vigorously anhydrous conditions. Indeed Stancheva *et al.* [3] report that attempts to synthesise Mn(NCSe)$_2$ in aqueous solution resulted only in the precipitation of selenium as a decomposition product. The synthesis from manganese(II) chloride and potassium selenocyanate in ethanol was therefore only attempted under rigorously anhydrous conditions. Once isolated, manganese(II) selenocyanate was found to be extremely sensitive to air, moisture and slightly light sensitive. It was therefore always stored *in vacuo*, in the dark. The infra-red spectrum of Mn(NCSe)$_2$ (Nujol mull, Table II) exhibits bands at 2100 and 2075 cm^{-1}. The latter may be readily assigned to ν(CN) of Mn–NCSe, but the former is of lower energy than would be expected for the Mn–NCSe–Mn linkage. The observed room temperature magnetic moment for Mn(NCSe)$_2$, μ_{eff} = 5.08 μ_B, is similar to that of Mn(NCS)$_2$, μ_{eff} = 5.20 μ_B; both are less than expected for high-spin 3d^5 systems, but are nonetheless consistent with some spin-pairing *via* the bridged anions in a polymeric structure. Thus, whilst the reduced magnetic moment of Mn(NCSe)$_2$ is consistent with a bridged anion system, the structures of Mn(NCSe)$_2$ and Mn(NCS)$_2$ are undoubtedly different.

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*Author to whom correspondence should be addressed.

⁺Permanent address: Department of Chemistry, UMIST, Manchester M60 1QD, U.K.

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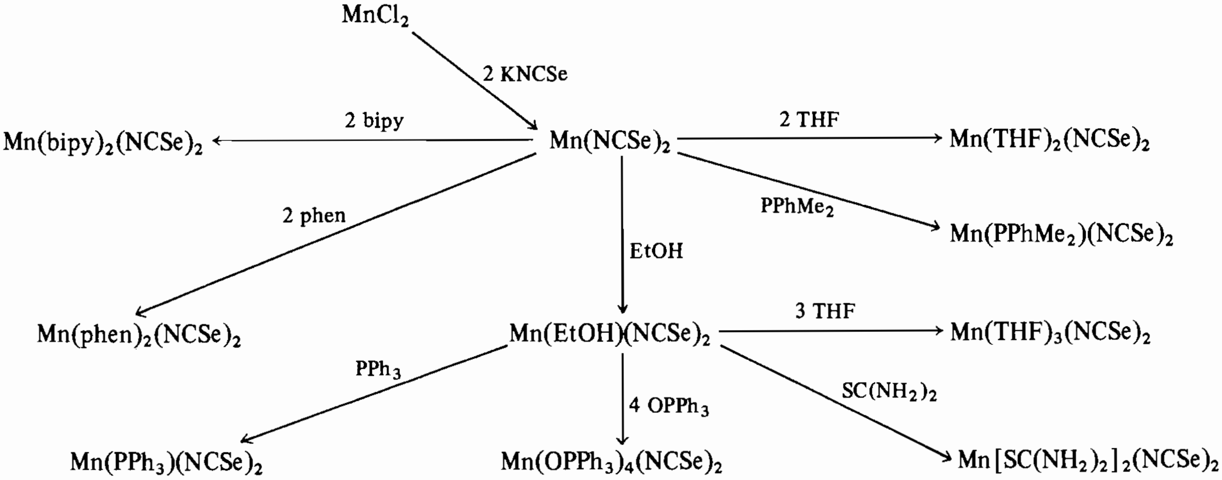
TABLE I. Elemental Analyses of the Manganese(II) Selenocyanate Complexes.

Compound	Colour	% C^{a}	% H^{a}	% N^{a}	% P^{a}	% Mn^{a}
$Mn(NCSe)_2$	white/pink	9.0(9.0)		10.0(10.5)		21.1(20.8)
$Mn(EtOH)(NCSe)_2$	cream	15.1(15.4)	1.9(1.9)	8.8(9.0)		16.9(17.7)
$Mn(THF)_2(NCSe)_2$	white/yellow	29.5(29.4)	4.4(3.9)	6.4(6.9)		13.5(13.5)
$Mn(PPhMe_2)(NCSe)_2$	pink/white	29.8(29.2)	2.4(2.7)	7.6(7.0)	7.4(7.7)	13.3(13.6)
$Mn(PPh_3(NCSe)_2$	cream	46.9(45.5)	3.3(2.9)	4.8(5.3)	5.8(5.9)	10.1(10.4)
$Mn(phen)_2(NCSe)_2$	pale green	50.1(49.9)	2.3(2.6)	13.3(13.4)		8.6(8.8)
$Mn(bipy)_2(NCSe)_2$	pale yellow	45.8(45.7)	2.5(2.8)	14.3(14.6)		9.3(9.5)
$Mn[SC(NH_2)_2]_2(NCSe)_2$	white	12.0(11.5)	2.2(1.9)	20.0(20.1)		12.4(13.2)
$Mn(THF)_3(NCSe)_2$	cream	34.4(34.9)	4.8(5.0)	6.0(5.8)		11.9(11.4)
$Mn(OPPh_3)_4(NCSe)_2$	white	64.5(64.5)	4.4(4.4)	2.1(2.0)		4.0(4.0)

[a] Found (Calculated).



Scheme: Preparative reactions for mixed ligand complexes of manganese(II) selenocyanate

TABLE II. Infrared Spectral Assignments for the Manganese(II) Selenocyanate Complexes (cm^{-1}).

Compound	ν(C–N)	ν(C–S)	ν(NCSe)	ν(Mn–N)	ν(Mn–O)	ν(ligand)
$Mn(NCSe)_2$	2100s 2075sh	600w 570w	443m	238s		
$Mn(EtOH)(NCSe)_2$	2100sh 2090s	610w	440w 410w	239s	418w 323m	3320s^{a}
$Mn(THF)_2(NCSe)_2$	2075s	660w	430m	238s		1040s^{b} 830m^{b}
$Mn(PPhMe_2)(NCSe)_2$	2140sh 2100s 2075sh	610w	470w 410w	240m		1437^{c} 417^{d}
$Mn(PPh_3)(NCSe)_2$	2140sh 2100s 2070sh	615m	465w 420w	232m		1432^{c} 416^{d}
$Mn(phen)(NCSe)_2$	2054s 2050sh	630m 637m	454w	252sh 240s		1585w^{e}
$Mn(bipy)_2(NCSe)_2$	2040s 2038sh	635m 630sh	460w	246sh 226s		1590m^{e}

(continued on facing page)

TABLE II *(continued)*

Compound	ν(C–N)	ν(C–S)	ν(NCSe)	ν(Mn–N)	ν(Mn–O)	ν(ligand)
$Mn(OPPh_3)_4(NCSe)_2$	2087sh 2079s 2065sh	620w		255s	406m 322s 302s	1171s^f
$Mn[SC(NH_2)_2]_2(NCSe)_2$	2050s	650w	445w	264s		3350s^g 3250s^g 3160s^g 1610s^h
$Mn(THF)_3(NCSe)_2$	2075s	610w		237s	419m 300w	1020m^b 875m^b

$^a\nu$(OH). $^b\nu$(COC). $^c\nu$(CP). $^d\nu$(Mn–P). $^e\nu$(C–N$_{Ar}$). $^f\nu$(P=O). $^g\nu$(NH). $^h\nu$(C=S).

For anhydrous $Mn(NCS)_2$ only a single very sharp ν(CN) band at 2120 cm^{-1} is observed, whereas two bands are observed for the selenocyanate salt, one of which is the low energy terminal Mn–NCSe band.

The X-band powder ESR spectrum of $Mn(NCSe)_2$ at room temperature (Fig. 1) and that of $Mn(PPhMe_2)(NCSe)_2$ (see later) are very unusual; no spectra of this type have previously been reported for high-spin d^5 systems. The spectrum resembles that expected for a 3d^2 ion in a tetrahedral crystal field or a 3d^8 ion in an octahedral crystal field. For these ions, the sharp line is due to a double quantum transition superimposed on the broad $g = 2$ peak, $\Delta M_s = \pm 1$ transitions observed by the splitting of the $^3A_{2g}$ ground state in the applied magnetic field [8]. However, it is not possible to envisage any stable structure which has a manganese centre with the same ground state.

The $^6A_1$ ground state would not be expected to yield transitions similar to those observed for the d^2 and d^8 ions, and it may be that the observed phenomena are related to the $\Delta M_I = \pm 1$ forbidden transitions occasionally observed in the ESR spectra of manganese(II) complexes [9].

Some photochemical behavior relevant to the synthesis of $Mn(NCSe)_2$ and $Mn(EtOH)(NCSe)_2$ has been observed. Thus, from an ethanolic solution of $Mn(NCSe)_2$ stored in daylight the simple $Mn(NCSe)_2$ salt can be isolated. Storing the solution in the dark, however, allows the deposition of the microcrystalline $Mn(EtOH)(NCSe)_2$. The infra-red spectrum of the latter (Table II) shows evidence for co-ordinated ethanol, the ν(OH) band being sharpened and shifted 30 cm^{-1} to lower energy from that of free EtOH. The ESR spectrum of the complex is quite different from that of $Mn(NCSe)_2$, exhibiting only a strong, broad signal at $g = 2$. Thus, while this does give some additional evidence for ethanol co-ordination, it gives little indication as to the co-ordination geometry about the manganese atom. Some evidence is, however, available from the infra-red spectrum (Table II), which exhibits bands assignable to both bridging Mn–NCSe–Mn and terminal Mn–NCSe linkages, and thus strongly suggests structure (I).

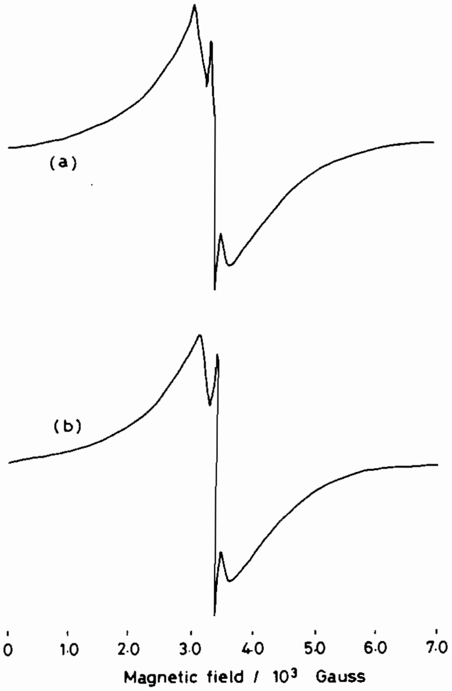
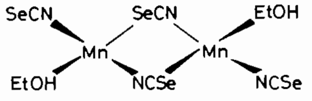
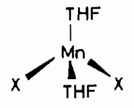


Fig. 1. Room temperature powder X-band ESR. Spectra of (a) $Mn(NCSe)_2$ and (b) $Mn(PPhMe_2)(NCSe)_2$.

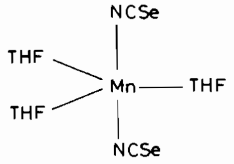
The infra-red spectrum of $Mn(THF)_2(NCSe)_2$ shows only a single band due to ν(CN) at 2075 cm^{-1}. This strongly suggests the presence of only one type of terminal Mn–NCSe environment. Thus it seems likely that $Mn(THF)_2(NCS)_2$ and $Mn(THF)_2(NCSe)_2$ are isostructural (see II), both being pseudo-tetrahedral monomers. Bonds assignable to ν(C–O–C) are also exhibited at 1040 and 880 cm^{-1} and are indicative of co-ordinated THF [11] (Table II). The ESR spectrum exhibits only a single peak at $g = 2$ yielding no unambiguous structural information.



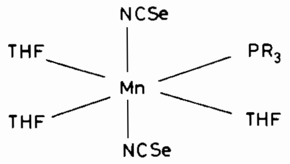
(I)



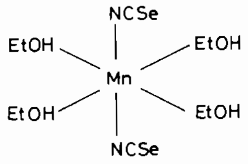
(II)



(III)



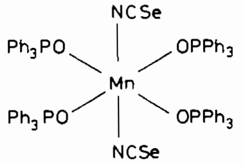
(IV)



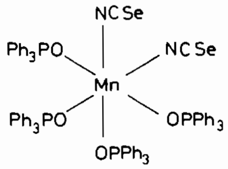
(V)

$[Mn(OPPh_3)_4](ClO_4)_2$

(VIa)



(VIb)



(VIc)

The complex $Mn(THF)_3(NCSe)_2$ had previously been isolated by Stancheva *et al.* [3], but no information was presented by these authors about whether the THF was co-ordinated or not. The method used by us in the preparation in $Mn(THF)(NCSe)_2$, starting from $Mn(EtOH)(NCSe)_2$ (see Scheme) was also different from that of earlier workers [3]. A single ν(CN) absorption in the infra-red spectrum at 2075 cm^{-1} strongly suggests the presence of only one type of terminal Mn–NCSe environment (Table II), whilst ν(C–O–C) bands at 1020 and 875 cm^{-1} are indicative of co-ordinated THF [11]. Although the ESR spectrum, which only exhibits a single intense peak at g = 2, provides no unambiguous structural information, all available evidence points to a monomeric structure(III) in which there are no bridging ligands and, since the infra-red bands characteristic of Mn–NCSe and Mn–O(THF) are sharp, each of the two different types of ligand are probably in identical environments.

Only the trigonal bipyramidal structure(III) is consistent with the available evidence; and this is the structure first suggested for this compound by Norbury [12].

It has previously been shown that the complexes $[M\{SC(NH_2)_2\}_2(NCS)_2]$ (M = Mn, Ni) are isostructural [13], containing bridging -NCS- ligands. In the apparently analogous $Mn\{SC(NH_2)_2\}_2(NCSe)_2$ complex prepared here, however, whilst there is evidence for co-ordinated thiourea (Table II), the low energy of ν(CN) for the selenocyanate, 2050 cm^{-1}, is strong evidence for the presence of only terminal Mn–NCSe bonds [12] and this complex is thus not isostructural with the thiocyanate analogue.

Complexes of formula $Mn(PR_3)X_2$ (X = Cl, Br, I, NCS) have previously been reported [6, 14–19] and the majority of these have been found to be capable of reversibly co-ordinating small molecules, most notably dioxygen. Here we have prepared $Mn(PPh_3)(NCSe)_2$ and $Mn(PPhMe_2)(NCSe)_2$, the former from $Mn(EtOH)(NCSe)_2$ and the latter from $Mn(NCSe)_2$ (Scheme). Thus, whilst it is possible to prepare these complexes either from the simple salt or its solvento-adduct, it was observed that a cleaner, simpler reaction occurred using $Mn(EtOH)(NCSe)_2$. This reaction:

$$Mn(EtOH)(NCSe)_2 + PPh_3 \xrightarrow{\text{toluene}} Mn(PPh_3)(NCSe)_2 + EtOH$$

is interesting as it represents the substitution at manganese(II) of an oxygen-bonded ligand by a tertiary phosphine.

However, whilst both complexes have the same stoichiometry, spectroscopic measurements do show some structural differences. Since $Mn(NCSe)_2$ has ν(CN) at 2100 cm^{-1}, and which is presumably evidence of bridging Mn–NCSe–MN groups, then bands at 2100 cm^{-1} in $Mn(PPhMe_2)(NCSe)_2$ and $Mn(PPh_3)(NCSe)_2$ probably also reflect the presence of this linkage. The ESR spectra point to differences, however: $Mn(PPh_3)(NCSe)_2$ gives a single intense peak at g = 2 in the solid state at room temperature, but the spectrum in frozen THF at 93 K is very complex being similar to a typical ESR spectrum of an $Mn(PR_3)(NCS)_2$ complex in THF, (Fig. 2). This suggests a pseudo-octahedral structure in THF solution (IV).

The room temperature, powder ESR spectrum of $Mn(PPhMe_2)(NCSe)_2$, however, is somewhat different (Fig. 1), being similar to $Mn(NCSe)_2$, thus further highlighting the differences between $Mn(PPh_3)(NCSe)_2$ and $Mn(PPhMe_2(NCSe)_2$.

Neither $Mn(PPh_3)(NCSe)_2$ or $Mn(PPhMe_2)(NCSe)_2$ exhibit any ability to co-ordinate dioxygen under ambient conditions. It has previously been pointed out [1] that the ability or otherwise of the thiocyanate series, $Mn(PR_3)(NCS)_2$ to bind dioxygen is mirrored in the energies and profile of the ν(C–N) bands. More specifically, O_2-binding activity is not seen when a very high energy, 2140–2115 cm^{-1}, band is present. This appears to also occur in the

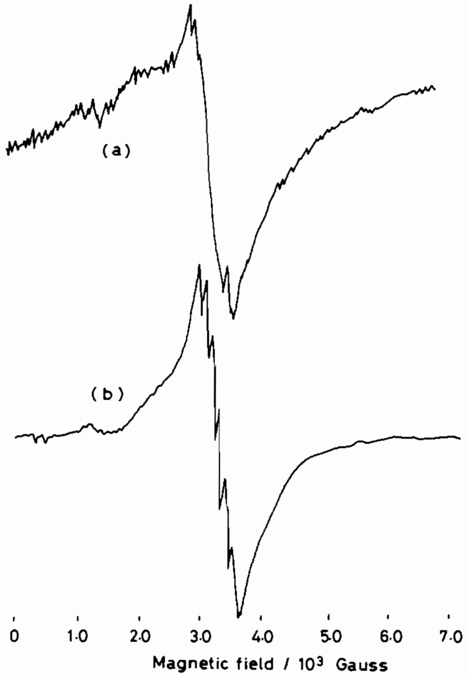


Fig. 2. X-band ESR spectra of (a) $Mn(PPh_3)(NCSe)_2$ and (b) $Mn(P(C_5H_{11})_3)(NCSe)_2$ (included for comparison) in frozen tetrahydrofuran at 93 K.

$Mn(PR_3(NCSe)_2$ complexes, for both of the complexes reported here which are inactive, exhibit bands at 2140 cm^{-1} (Table II).

The ESR spectrum of an ethanolic solution of $Mn(NCSe)_2$ (Fig. 3) at 93 K shows a large number of absorptions characteristic of a high-spin (^6S) manganese(II) species with intermediate zero-field splitting ($D < 0.3$ cm^{-1}). However, accurate values of D and λ (the ratio of the zero-field splitting parameters, $= E/D$) cannot be determined without computer simulation of the spectrum. Hence, the structure of the species present in solution is unclear, but it seems likely that the complex adopts a *trans*-octahedral structure (V) in ethanol solution.

The ESR spectrum of $Mn(OPPh_3)_4(NCSe)_2$ (Fig. 3) shows a large number of absorptions in the region 600–5050 G indicative of a small D value (<0.3 cm^{-1}). The number of absorptions in this region is more than would be expected for any one value of λ and D as computed initially for along-axis transitions [20], and thus, by implication, to any one species. However, the limitations of the published D/B curves [20] have been discussed [21]. In particular, more absorptions can appear in the experimental spectrum than would be expected on examination of the D/B curves alone, due to the possibility of off-axis transitions also occurring for low values of D.

The infra-red spectrum of $Mn(OPPh_3)_4(NCSe)_2$ (Table II) is consistent with more than one species being present but, although the ESR does not rule out this possibility, without computer simulation of the spectrum, it does not provide definite evidence. Of the three likely isomeric possibilities (VIa, VIb, VIc), VIa, which occurs in $[Mn(OPPh_3)_4]ClO_4)_2$ [22], can be ruled out, since there is no evidence in the infra-red spectrum for free $NCSe^-$ [12]. Thus, VIb and VIc are the isomers most likely to be present. One ν(CN) absorption is expected for VIb and two for VIc, and the occurrence of three bands close in energy strongly suggests that the complex precipitates out as both *cis* and *trans*-$[Mn(OPPh_3)_4(NCSe)_2]$.

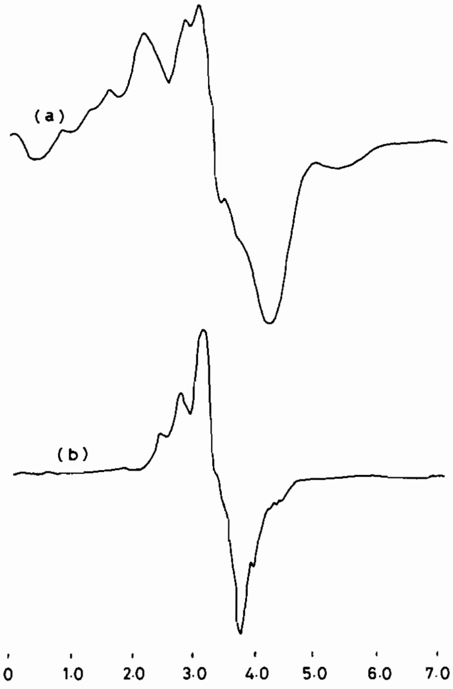


Fig. 3. X-band ESR spectra of (a) ethanol glass of $Mn(NCSe)_2$ at 93 K, and (b) powdered $Mn(OPPh_3)_4(NCSe)_2$ at room temperature.

Goodgame, Goodgame and Hayward [21] have assigned a *cis*-arrangement of thiocyanate groups of $Mn(o\text{-phen})(NCS)_2$. The ESR spectrum of $Mn(o\text{-phen})(NCSe)_2$ (Fig. 4) is similar to that of the isothiocyanate analogue, and the infrared spectrum (Table II) is consistent with a *cis*-arrangement [3] of isoselenocyanate ligands. The ESR spectrum of $Mn(bipy)(NCSe)_2$ (Fig. 4) is also similar, giving a low value for D, and ν(CN) and ν(CSe) doublets in the infrared spectrum is further evidence for a *cis* structure.

Experimental

Reagents

Tetrahydrofuran (THF) (Aldrich Chemical Co.) was refluxed over *ca.* 50.0 g of potassium metal and

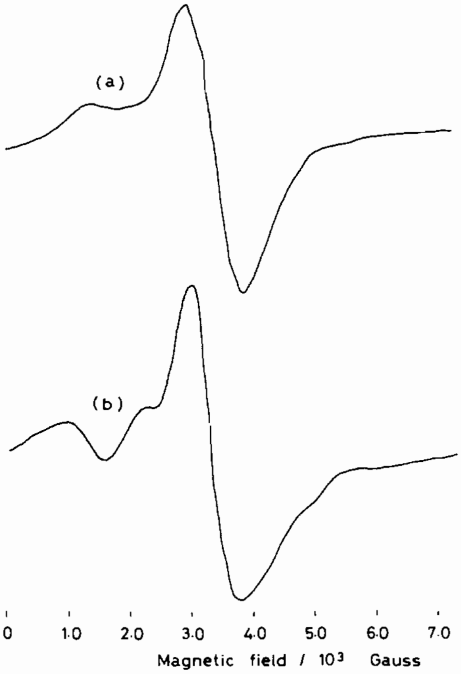


Fig. 4. Room temperature powder X-band ESR spectra of (a) Mn(bipy)$_2$(NCSe)$_2$ and (b) Mn(phen)$_2$(NCSe)$_2$.

10.0 g benzophenone in a 3 litre flask fitted with a modified take-off head and double surface condenser. A continuous stream of dry dinitrogen was passed through the THF solution to keep the solvent free of dioxygen and prevent 'bumping'. After *ca.* 5 hours the THF solution attained a blue/purple colour (due to the formation of potassium benzophenone ketyl) indicating that the solvent was free of both moisture and dioxygen. The dry THF was distilled as required, *via* the modified take-off head, into dry, dinitrogen filled flasks.

Toluene (Fisons, Analar grade) was dried in a similar manner to THF; however, sodium was used in place of potassium. In general the toluene was freshly distilled as required but in certain cases it was stored over dry, freshly degassed 4A molecular sieves under a dry dinitrogen atmosphere for a maximum of one week.

Ethanol (BDH reagent grade), was dried using the standard method [23]. To 1.0 g magnesium turnings in a 1 litre flask, 200 cm^3 ethanol and 0.1 g iodine were added. The mixture was refluxed for *ca.* 24 hours until a white/grey colour was attained; 800 cm^3 ethanol were further added and the mixture refluxed for a further hour. The dry ethanol was freshly distilled into dry dinitrogen filled flasks as required.

Chlorinated hydrocarbons were distilled over P_4O_{10} under a dry dinitrogen atmosphere. The first 10% was discarded, the remaining distillate was stored over dry, freshly degassed 4A molecular sieves.

Synthesis of Mn(L)$_n$(NCSe)$_2$ Complexes

Mn(NCSe)$_2$ and Mn(EtOH)(NCSe)$_2$

1.0 g (7.9 mmol) of anhydrous MnCl$_2$ was dissolved in 80 cm^3 dry ethanol. 2.3 g (15.8 mmol) KNCSe (BDH Ltd.; recrystallised) was added to the mixture with the immediate precipitation of KCl. The mixture was stirred for 24 hours and filtered using a Schlenk apparatus. The resulting filtrate was concentrated *in vacuo* and on addition of dry diethyl ether a white precipitate of Mn(NCSe)$_2$ was obtained. This was filtered using a Schlenk apparatus and dried *in vacuo.* On standing in the dark, the concentrated filtrate produced small crystals of Mn(EtOH)(NCSe)$_2$, which was filtered using a Schlenk apparatus and dried *in vacuo.* However, if the solution was allowed to stand in daylight, the unsolvated Mn(NCSe)$_2$ was obtained. After isolation, however, Mn(NCSe)$_2$ must be stored in the dark *in vacuo.*

Mn(PPh$_3$)(NCSe)$_2$ and Mn(PPhMe$_2$)(NCSe)$_2$

The procedures used in the synthesis of Mn(PPh$_3$)(NCSe$_2$) and Mn(PPhMe$_2$)(NCSe)$_2$ were essentially the same except that Mn(PPh$_3$)(NCSe)$_2$ was prepared from Mn(EtOH)(NCSe)$_2$, whereas Mn(PPhMe$_2$)(NCSe)$_2$ was prepared from Mn(NCSe)$_2$. The procedure for the synthesis of Mn(PPh$_3$)(NCSe)$_2$ is described here.

0.35 g (1.1 mmol) of Mn(EtOH)(NCSe)$_2$ was added to 50 cm^3 of dry toluene in a dry 250 cm^3 side-arm flask. 0.29 g (1.1 mmol) of PPh$_3$ were added and the mixture stirred for 72 hours. The resulting cream coloured complex was filtered using a Schlenk apparatus and dried *in vacuo.*

Mn(THF)$_2$(NCSe)$_2$ and Mn(THF)$_3$(NCSe)$_2$

The procedures for the synthesis of Mn(THF)$_2$(NCSe)$_2$ and Mn(THF)$_3$(NCSe)$_2$ were essentially the same except that Mn(THF)$_3$(NCSe)$_2$ was prepared from Mn(EtOH)(NCSe)$_2$. The procedure for the synthesis of Mn(THF)$_2$(NCSe)$_2$ is described here.

0.2 g (0.8 mmol) of Mn(NCSe)$_2$ was added to 20 cm^3 of dry THF in a dry 250 cm^3 side-arm flask. The mixture was stirred for *ca.* 24 hours and the resulting pale pink solid filtered using a Schlenk apparatus and dried *in vacuo.*

Mn(L)$_n$(NCSe)$_2$ Complexes ($n = 2$, L = SC(NH$_2$)$_2$, bipy, phen; $n = 4$, L = OPPh$_3$)

The procedures used in the synthesis of all these complexes were essentially the same. The procedure used in the synthesis of Mn(OPPh$_3$)$_4$(NCSe)$_2$ is described here.

0.5 g (1.6 mmol) of Mn(EtOH)(NCSe)$_2$ was dissolved in 50 cm^3 of dry ethanol in a dry 250 cm^3 side-arm flask. 1.79 g (6.4 mmol) of OPPh$_3$ was dissolved in 20 cm^3 of hot (*ca.* 60 °C), dry ethanol and added to the solution. A white precipitate of

$Mn(OPPh_3)_4(NCSe)_2$ was immediately produced which was filtered using a Schlenk apparatus and dried *in vacuo*.

Physical Measurements were obtained as previously described [24].

References

1 Part 11. C. A. McAuliffe, C. G. Benson and S. P. Tanner, *J.C.S. Dalton*, paper submitted for publication. Part 12. C. A. McAuliffe and K. Minten, *J.C.S. Dalton*, submitted for publication.

2 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry', Wiley Interscience, New York, 3rd Ed., p. 847 (1972).

3 P. Stancheva, V. V. Skopenko and G. V. Tsintsadze, *Ukr. Khim. Zh., 35*, 166 (1969).

4 D. Forster and D. M. L. Goodgame, *Inorg. Chem., 4*, 1712 (1965).

5 J. L. Burmeister and L. E. Williams, *Inorg. Chem., 5*, 1113 (1966).

6 C. A. McAuliffe, H. Al-Khateeb, D. S. Barratt, J. C. Briggs, A. Challita, A. Hosseiny, M. G. Little, A. G. Mackie and K. Minten, *J.C.S. Dalton*, 2147 (1983).

7 K. Minten, Ph.D. Thesis, University of Manchester, 1983.

8 J. E. Wertz and J. R. Bolton, 'Electron Spin Resonance: Elementary Theory and Applications', McGraw-Hill, New York, 1972, p. 289–295.

9 B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radiochem., 13*, 220 (1970).

10 A. Hosseiny, C. A. McAuliffe, K. Minten, M. J. Parrott, R. Pritchard and J. Tames, *Inorg. Chim. Acta, 39*, 227 (1980).

11 G. W. A. Fowles, D. A. Rice and R. A. Walton, *J. Inorg. Nucl. Chem., 31*, 3119 (1969).

12 A. H. Norbury, *Adv. Inorg. Chem. Radiochem., 17*, 231 (1975).

13 D. M. L. Goodgame and F. A. Cotton, *J. Chem. Soc.*, 3735 (1971).

14 C. A. McAuliffe, H. Al-Khateeb, M. H. Jones, W. Levason, K. Minten and F. P. McCullough, *J.C.S. Chem. Comm.*, 737 (1979).

15 M. Barber, R. S. Bordoli, A. Hosseiny, K. Minten, C. R. Perkin, R. D. Sedgwick and C. A. McAuliffe, *Inorg. Chim. Acta, 45*, L89 (1980).

16 M. Al-Khateeb and C. A. McAuliffe, *Inorg. Chim. Acta, 45*, L195 (1980).

17 A. Hosseiny, C. A. McAuliffe, A. G. Mackie and K. Minten, *Inorg. Chim. Acta, 49*, 99 (1981).

18 C. A. McAuliffe, *J. Organomet. Chem., 228*, 225 (1982).

19 M. G. Little, C. A. McAuliffe and J. B. Raynor, *J.C.S. Chem. Comm.*, 68 (1982).

20 R. D. Dowsing and J. F. Gibson, *J. Chem. Phys., 50*, 294 (1969).

21 J. F. Gibson, 'E.S.R. and N.M.R. of Paramagnetic Species in Biological and Related Systems', NATO Advanced Study Institute Series, I. Bertini and R. S. Drago, Eds., D. Reidel Publishing Co., Dordrecht, p. 225 (1979) and refs. therein.

22 D. M. L. Goodgame, M. Goodgame and P. J. Hayward, *J. Chem. Soc. (A)*, 1352 (1970).

23 A. Vogel, 'Vogel's Textbook of Practical Organic Chemistry', Longman, London, p. 269 (1978).

24 S. Haghighi, C. A. McAuliffe, W. E. Hill, H. H. Kohl and M. E. Friedman, *Inorg. Chim. Acta, 43*, 113 (1980).