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Manganese(II) thiocyanate complexes with bis(phosphine oxide) ligands: synthesis and excitation wavelength-dependent multicolor luminescence

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First examples of luminescent Mn^{II} thiocyanate complexes are presented. A series of such compounds has been synthesized *via* the reaction of $Mn(NCS)_2$ with bis(phosphine oxides), $Ph_2P(O)-X-(O)PPh_2$, where $X = CH_2$ (**L1**), CH_2CH_2 (**L2**), $CH_2CH_2CH_2$ (**L3**), $CH_2C(=CH_2)CH_2$ (**L4**), $C(=CH_2)C(=CH_2)$ (**L5**) and $C \equiv C$ (**L6**). The **L1**, **L3** and **L4** ligands, when reacted with $Mn(NCS)_2$ on air (EtOH/acetone, r.t.), produce chelate complexes $[Mn^{II}(O^{A}O)_2(NCS)_2]$. Under similar conditions, **L5** gives ionic complex $[Mn^{II}(L5)_3][Mn^{II}(NCS)_4]$, whereas **L6** affords chain coordination polymer (CP) $[Mn^{II}(L6)_2(NCS)_2]_n$. By contrast, ligand **L2** results in formation of mixed-valent chain CP $[Mn^{II}Mn^{III}(L2)_3(NCS)_5]_n$.

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Introduction

At present, Mn^{II} complexes and Mn^{II}-doped solids attract great attention due to their unique photo- and electroluminescent properties, low cost, high stability and facile processability.^[1] The luminescence of these materials is originated by spin-forbidden d-dtransitions within Mn2+ ion, has a phosphorescent character and covers the spectral range from ~500 nm to near-IR edge.^[1,2] Because of a strong sensitivity of Mn2+-based emission to ligand field strength and symmetry,^[1-3] its energy can be controlled via changing of the coordination geometry, whereas lifetime can be tuned by varying nature of the ligated atoms. The classical cases are represented by octahedral (O_h) and tetrahedral (T_d) ligand fields, in which Mn^{2+} ion emits in red (610–660 nm) and green (510–560 nm) regions, respectively.^[1-3] For example, the commonly known halomanganates [MnHal4]²⁻ display green luminescence,^[4-15] while the complexes of $[(L)MnHal_3]$ and $L_6[Mn_3Cl_{12}]$ type (L = protonated or alkylated N-base)^[16-22] and Mn²⁺-doped sulfide and oxide nanocrystals^[1, 23, 24] exhibit red emission. The compounds containing tetrahedral and octahedral Mn(II) centers, e.g. both [Mn(dppeO₂)₃]MnHal₄, manifest a dual emission.^[25] Moreover, unique thermochromic luminescence associated with conversion of a tetrahedronal to trigonal bipyramidal geometry of Mn²⁺ has been reported.[26]

Complex $[Mn(L4)_2(NCS)_2]$ and CP $[Mn(L6)_2(NCS)_2]_n$ display unique dual luminescence, i.e. the intraligand fluorescence (blue band) and Mn^{II}-centered phosphorescence (red band), the ratio of which is largely modulated by excitation wavelength. Through this feature, the luminescence color of these complexes can be smoothly tuned from **a** deep-blue to **a** red. Complex $[Mn(L5)_3][Mn(NCS)_4]$ shows Mn^{II}-based phosphorescence only.

Particular interest is devoted to Mn(II) halide complexes with phosphine oxide ligands.^[25, 27-37] For instance, some of them, e.g. [Mn(Ph₃PO)₂Br₂], exhibit bright photo- and triboluminescence at ambient temperature.^[27-31] The [Mn(DPEPhosO₂)Hal₂] complexes derived from DPEPhos dioxide were claimed as bright photo- and triboluminescent.^[32] An intriguing vapochromic luminescence was found for 1D coordination polymer [Mn(dppeO₂)Br₂]_n.^[33] More recently, utilizing adducts of MnCl2 and MnBr2 with 4,6bis(diphenylphosphoryl)dibenzofuran, first efficient Mn-based PhOLEDs were fabricated.^[34] By contrast, Mn(II) pseudohalide complexes supported by phosphine oxide ligands remain neglected, although they are also expected to be promising class of luminescent materials. In particular, among such Mn(II) thiocyanate complexes, only four examples were credibly described, *viz.* $[Mn(Ph_3PO)_2(NCS)Cl]$,^[38] $[(Ph_3PO)_2Mn \binom{scn}{NcS} Mn(Ph_3PO)_2]$,^[39] examples $[Mn(Ph_3PO)_4(NCS)_2]^{[39]}$ and $[Mn_2(\mu-dpppO_2)_4(NCS)_2](NCS)_2.^{[40]}$ To our knowledge, luminescence of any Mn thiocyanate complexes was not studied at all. Taking this into account, as well as the rich coordination abilities of the [NCS]⁻ ion,^[41] the development of new Mn(NCS)₂ complexes with phosphine oxide ligands is a major challenge in the context of access to novel emitting materials ranging from discrete compounds to complicated 3D frameworks.

Herein, aiming to reveal the potential of Mn thiocyanate compounds in terms of luminescence, we have investigated a series of Mn^{II} and $Mn^{II,III}$ complexes synthesized through the reaction of $Mn(NCS)_2$ with a set of the bis(phosphine oxide) ligands **L1–6** depicted in Scheme 1. Some of the resulting molecular complexes and coordination polymers (CPs), being essentially the first representatives of emissive Mn^{II} thiocyanate compounds, exhibit unique excitation wavelength-dependent dual luminescence at ambient temperature. From this viewpoint, the designed Mn-based dual emitting single molecule-based materials are promising platform for creation of new optoelectronic devices such as multicolor OLEDs, luminescent sensors and photoswitches.^[42-44]



Scheme 1. Structures of the studied bis(phosphine oxide) ligands L1-6.

Results and Discussion

Synthetic part

To disclose coordination abilities of ligands **L1–6** toward Mn(NCS)₂, a series of experiments has been carried out using various molar ratios of the reactants. The reactions have been performed in EtOH/acetone mixed solvent under ambient conditions (r.t., air, 1 h) with Mn(NCS)₂ generated *in situ* by the reaction of MnCl₂·4H₂O with NaNCS. The isolated products have been analyzed by single crystal (sc-XRD) and powder X-ray diffraction (PXRD) techniques, which have revealed the following regularities and peculiarities of the reaction (Scheme 2). So, ligands **L1, L3** and

L4 react with Mn(NCS)₂ to afford neutral bis-chelating complexes **1. 3** and **4** of a general formula $[Mn^{II}(O^{O})_2(NCS)_2]$. Meanwhile, ligand L5 under similar conditions provides ionic complex $[Mn^{II}(L5)_3][Mn^{II}(NCS)_4]$ (5), composed by tris-chelated cation and tetrahedrally-coordinated [Mn(NCS)4]²⁻ anion. The acetylene-based ligand L6 is found to be easily assembled with Mn(NCS)2 into 1D CP $[Mn^{II}(L6)_2(NCS)_2]_n$ (5), the adjacent Mn^{2+} ions of which are linked by two bridging ligands. The most surprising result is observed with 1,2-bis(diphenylphosphinyl)ethane (L2) that forms mixed-valent chain polymer $[Mn^{II}Mn^{III}(L2)_3(NCS)_5]_n$ (2). The latter is composed of Mn^{II}(NCS)₂ and Mn^{III}(NCS)₃ modules separated by bridging L2 ligands. The Mn^{III} ions within CP 2 are obviously resulted from oxidation of Mn(NCS)2 on air. This distinctive feature of L2 can tentatively be ascribed to its higher ability to stabilize Mn^{III}(NCS)₃ species as compared to other tested ligands. Moreover, the basicity of thiocyanate anions can also favor the formation of mixed valence Mn^{II}-Mn^{III} CP 2. Note that the terminal [NCS]⁻ anions in compounds 1-6 act as N-bonded ones that is in the line with HSAB concept and the literature data.^[38,39,41] It is relevant to note also that, apart from the titled bis(phosphine oxides), DPEPhosO₂ and 1,2,4,5-tetrakis(diphenylphosphinyl)benzene have been tested in the reaction with Mn(NCS)₂, but no X-ray quality crystals of products formed have been obtained.



Scheme 2. Reactions of Mn(NCS)₂ with bis(phosphine oxide) ligands L1-6. (Conditions: EtOH/acetone, r.t., air).

Compounds **1–6** have been isolated in 47–68% yield (nonoptimized) as air- and light-stable colorless solids, soluble in MeCN and CH₂Cl₂. Their phase purity has been validated by PXRD (Figs. S1–6) and microanalyses data. FT-IR spectra of **1–6** in middle region well agree with available X-ray structures, demonstrating vibrations of the organic ligand's skeleton (Figure S7). The asymmetric stretching vibrations of the thiocyanate anions (v_{CN}) appear as a strong band at ~ 2065–2077 cm⁻¹, thus confirming their terminal *N*-bonded pattern.^[45]

Crystal structures

Complex 1 crystallizes from DMF as solvate 1.2DMF showing molecular structure. The metal atom has an octahedral environment composed of four oxygen atoms of the chelating ligands L1 and two nitrogen atoms of $[NCS]^-$ groups (Fig. 1). Since the latter are mutually adjacent within $[Mn@O_4N_2]$ octahedra, complex 1 can be considered as *cis*-isomer. One of the *N*-bonded terminal $[NCS]^$ anions is roughly linear, whereas the second one is slightly bended. The Mn–O (av. 2.206 Å) and Mn–N (av. 2.167 Å) distances are comparable with those of Mn^{II} complexes.^[38-40] In general, bond lengths and angles in the [Mn(NCS)₂] unit of **1** are consistent with those found in complexes **2–6** and in the related compounds reported earlier.^[38,39,46-49]



Figure 1. Molecular structure of 1·2DMF. Hydrogen atoms and solvate molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Mn1–N1 2.153(2), Mn1–N2 2.182(2), Mn1–O4 2.1827(13), Mn1–O1 2.1873(13), Mn1–O2 2.2192(14), Mn1–O3 2.2371(14); O4–Mn1–O1 165.11(5), N2–Mn1–O2 177.49(7), N1–Mn1–O3 174.63(7).

1D structure of CP **2** is represented by zig-zag chains built up by alternating $Mn^{II}(NCS)_2$ and $Mn^{II}(NCS)_3$ units, bridged by the O=P(Ph₂)CH₂CH₂(Ph₂)P=O linkers in a [-Mn^{II}-L2

positions. Note that the Mn^{III}–O bond lengths (av. 2.080 Å) are shorter as compared to Mn^{II}–O (av. 2.182 Å) ones. The similar trend is observed for Mn^{III}–N (ca. 2.100–2.183 Å) and Mn^{II}–N (ca. 2.195 and 2.285 Å) distances.

Compounds **3** and **4** reveal nearly superimposable molecular structures (Figs. 3 and 4) that differ only by middle atom in the ligand chains (CH₂ versus C=CH₂, accordingly). In terms of chemical bonding, both complexes resemble **1**, but in contrary to the latter, they are *trans*-isomers. Apparently, *cis*-isomers of **3** and **4** are energetically less preferable because of a higher steric hindrance entailed by the neighboring ligands **L3** and **L4**. At the same time, a smaller structure of **L1** does not prevent existence of **1** in the *cis*-form.



Figure 3. Molecular structure of **3**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Mn1–O2 2.178(4), Mn1–O1 2.185(4), Mn1–N1 2.212(5); O2–Mn1–O1 172.97(15), N1–Mn1–N1 179.7(3). Symmetry code: ([^]) –x, y, 1.5–z.



Figure 2. A fragment of the CP **2**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Mn1–O 2 2.078(2), Mn1–O1 2.082(3), Mn1–N2 2.099(4), Mn1–N1 2.152(4), Mn1–N4 2.183(4), Mn2–O5 2.157(2), Mn2–O6 2.177(2), Mn2–O3 2.188(2), Mn2–N3 2.195(3), Mn2–O4 2.207(2), Mn2–N5 2.285(3); O2–Mn1–O1 128.34(16), O2–Mn1–N2 123.08(15), N1–Mn1–N4 170.26(18), O3–Mn2–N3 166.75(10), O6–Mn2–O4 175.05(8), O5–Mn2–N5 179.77(10). Symmetry codes: (´) 2–x, –y, 1–z; (´´) 1–x, –1–y, 2–z.

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Figure 4. Molecular structure of 4. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Mn1–O2 2.1835(13), Mn1–O1

2.1990(12), Mn1-N1 2.2249(18); O2-Mn1-O1 173.44(5), N1-Mn1-N1

Ionic complex **5** is formed by tris-chelated $[Mn(L5)_3]^{2+}$ cations and $[Mn(NCS)_4]^{2-}$ anions (Fig. 5). In $[Mn(L5)_3]^{2+}$, metal atom lies

in the distorted octahedral surroundings with the Mn-O distances

varying from 2.131 to 2.168 Å. On the whole, geometry of the cation

is close to that of the related [Mn(L5)₃]MnBr₄ complex.^[25] The

 $[Mn(NCS)_4]^{2-}$ anion of **5** features tetrahedral geometry of Mn atom ($\tau_4 = 0.96^{[50]}$). The [NCS]⁻ groups are virtually linear and bonded

with metal so that Mn-N-C angle is ~167.84° that is consistent with

179.93(9). Symmetry code: (´) 2-x, y, 0.5-z.

the literature data.^[51-53]

S1 N1 atro N3 S3 O2 Min t O6 S2 O1 0 S2 O2 Min t O6

Figure 5. Molecular structure of 5. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Mn1–O4 2.1311(16), Mn1–O1 2.1395(16), Mn1–O2 2.1446(16), Mn1–O3 2.1476(16), Mn1–O6 2.1684(15), Mn1–O5 2.1676(16), Mn2–N3 2.033(4), Mn2–N4 2.037(3), Mn2–N1 2.051(4), Mn2–N2 2.075(4); O4–Mn1–O1 172.42(7), O2–Mn1–O3 170.44(7), O6–Mn1–O5 173.29(7), N3–Mn2–N4 104.99(16), N3–Mn2–N1 111.24(17), N4–Mn2–N1 110.78(13), N3–Mn2–N2 107.55(17), N4–Mn2–N2 113.23(16), N1–Mn2–N2 108.99(15).

1D chains of CP **5** are assembled by repeating Mn(NCS)₂ moieties, which are bridged by ligands **L5** in a $[Mn(^{0,0}_{G^{,0}})Mn]$ manner (Fig. 6). In the formed fourteen-membered (Mn-O-P-C-C-P-O)₂ rings, two slightly bended P–C=C–P fragments are mutually crossed at the dihedral angle of -48.11°. The distance between acetylene units of these fragments (3.891 Å) is long for appearance of the possible transannular π - π interaction. Each Mn atom of **5** adopts a *trans*-[Mn@O4N₂] octahedral geometry with two axial thiocyanate nitrogen atoms. Again, whilst the Mn–NCS arms are little bended, the [NCS]⁻ anions are closely linear.



Figure 6. A fragment of the CP **6**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Mn1–N1 2.151(4), Mn1–O2 2.192(3), Mn1–O4 2.240(3), Mn2–O3 2.166(3), Mn2–N2 2.172(4), Mn2–O1 2.229(3); N1–Mn1–N1 180.0(2), O2–Mn1–O2 180.0, O4–Mn1–O4 180.00(13), O3–Mn2–O3 180.0, N2–Mn2–N2 180.0(2), O1–Mn2–O1 180.00(12). Symmetry codes: (') 2–x, 1–y, 1–z; ('') 1–x, 1–y, 1–z.

In crystal packing of **1**, **3** and **4**, the closest Mn…Mn distances (11.423, 10.725 and 10.692 Å, respectively) are quite long in terms of possible Förster resonance energy transfer (FRET) from an photoexcited Mn^{2+} ion to neighboring nonexcited Mn^{2+} ion. Meanwhile, for compounds **2**, **5** and **6**, where these distances are shorter than 10 Å (8.683, 9.234 and 8.968 Å), the FRET channel may contribute to the luminescence properties.^[25]

Thermal properties

The TGA/DTG study evidences that compounds 3-6 are thermally stable up to ~ 280 °C, beginning from which one- or two-

step decomposition starts (Fig. 7). A similar pattern is also inherent in complex **1** that is formed upon desolvation of the parent solvate **1**·2DMF (*ca.* 170 °C). CP **2** appears to be the least stable and starts to decompose from 140 °C. The observed mass change at this step ($\Delta m_{obs} = 7.00\%$) corresponds to the loss of two "SCN" units from **2** ($\Delta m_{cald} = 6.86\%$). Keeping this in mind, we have assumed that the stage is associated with an intramolecular reduction of Mn^{III}(NCS)₃ modules of **2** leading to Mn^{II}(NCS)₂ ones and thiocyanogen (SCN)₂ degradation products.



Figure 7. TGA and DTA curves of 1-6.

Photoluminescent properties

The photophysical measurements have revealed a weak solid-state luminescence for compounds **4–6** at ambient temperature. Complexes **1–3** are essentially non-emissive. However, despite the low quantum efficiency (Φ_{PL} of **4–6** are 1%, 2% and 1%, respectively), complexes **4** and **6** are characterized by a unique multicolor emission expressed by two complementing bands, the ratio of which is sensitive to the excitation wavelength. It is relevant to note in this regard that the Mn-based multicolor emitting materials are still very limited,^[25, 36] although they are high-demand for the creation of low-cost white OLEDs of next generation as well as new photoswitches and sensing devices. UV-Vis spectra of the compounds **4–6** dissolved in acetonitrile are very similar showing a strong absorption band expanding from *far*-UV edge to 220 nm as well as two weaker bands maximized at ~ 225 and 270 nm (Fig. S8). The high-energy band has been assigned to π - π * transitions within phenyl groups of the ligands, while the lower-energy bands have been tentatively ascribed to Mn²⁺-centered spin-forbidden *d*-*d* transitions.

The emission spectra of polycrystalline 4 are presented by broad fluorescence and phosphorescence bands at ~ 420 nm and 670 nm, accordingly. The vibronically-structured shape of the high-energy band with $\Delta k_{av} \approx 1100 \text{ cm}^{-1}$ implies participation of the π -orbitals of the phenyl groups of L4 in emissive transitions. Indeed, the nanosecond order of the lifetimes determined for this band ($\tau_1 = 6.3$ ns, $\tau_2 = 176$ ns) corroborates its fluorescent origin. The decay kinetics of the low-energy emission band shows rather long lifetime of 0.92 ms that is typical for spin-forbidden ${}^{4}T_{1}(G) \rightarrow {}^{6}A_{1}$ transitions in Mn²⁺ ions located in octahedral ligand field.^[1-3, 25] The excitation spectrum of 4 (Fig. 8a), monitored for the phosphorescence band, features broad unresolved bands of Mn²⁺ ion terms. The excitation profile of the fluorescent band is a broad structureless band (covered 250–420 nm region) that can be arisen from $\pi \rightarrow \pi^*$ transitions in coordinated ligand L4. Note that the position and ratio of the red and blue bands are largely modulated by excitation energy. This excitation wavelength dependent behavior of 4 is remarkable since it allows fine-tuning the color of the luminescence through slight changing of the excitations. As illustrated by CIE chromaticity diagram (Fig. 9), a gradual increase of the excitation wavelengths from 280 to 400 nm leads to a smooth changing of the emitting light color from red to green.



Figure 8. (*left*) Excitation spectrum for solid complex 4 recorded at $\lambda_{em} = 450$ and 675 nm; (*right*) emission spectra of 4 recorded at different excitations ($\lambda_{ex} = 280-400$ nm).



Figure 9. CIE-1931 chromaticity diagram illustrating a change of the emission color of solid 4 upon varying of excitation wavelength.

310 nm

330 nm

350 nm

370 nm

390 nm

640

Wavelength (nm)

720

800

300 nm

320 nm

340 nm

360 nm

380 nm

400 nm

480

560

Intensity (a.u.)

2

400

A very similar dual luminescence has also been recognized for CP 6 demonstrating intraligand fluorescence and Mn^{II}-centered phosphorescence bands at ~ 440-460 nm and 730 nm, respectively (Fig. 10a). Again, the ratio of these components strongly depends upon the excitation wavelength. In contrast to 4, however, dual emission of 6 persists up to 340 nm excitation, and upon further increase in wavelength excitation, only blue band remains. This behavior is in line with the excitation profile of the low-energy emission band of 4 that demonstrates very weak intensity beginning with ~ 370 nm (Fig. S13). By contrast, excitation curve recorded for the high-energy emission band remains intensive up to ~ 420 nm (Fig. S13). Owing to this feature, as well as longer wavelength position of the phosphorescence band (730 nm, close to NIR domain), luminescence chromaticity of 6 can be tuned in a wider visible range: from a deep blue to a red (Fig. 10b). It should also be remarked that phosphorescence lifetime of 6 being 21.5 µs is unusually short for the emitting ${}^{4}T_{1}(G) \rightarrow {}^{6}A_{1}$ transition in Mn²⁺ ion,^[1, 16-25] whereas the fluorescence lifetime is normal ($\tau_1 = 1.2$ ns, $\tau_2 = 11.5$ ns).



Figure 10. (*left*) Emission spectra of solid 6 recorded at different excitations ($\lambda_{ex} = 300-400 \text{ nm}$); (*right*) CIE-1931 chromaticity diagram illustrating a change of the emission colour of 6 upon varying of excitation wavelength.

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Emission spectrum of $[Mn(L5)_3][Mn(NCS)_4]$ (5) that incorporates two potentially emitting Mn^{2+} ions, is dominated by red emission typical for octahedral Mn^{2+} ions (Fig. 11). The specific green luminescence originated from d-d transitions in $[Mn(NCS)_4]^{2-}$ anion appears at ambient temperature as a weak shoulder at 511 nm upon excitation with 300 nm light. The suppression of the green emission of the tetrahedral Mn^{2+} ions of 5 may be ascribed to effective Förster energy transfer from the $[Mn(NCS)_4]^{2-}$ anion to $[Mn(L5)_3]^{2+}$ cation that further emits the transferred energy. Previously, a similar phenomenon was earlier proposed for the related "two-in-one" complexes, in which Mn^{2+} ions in T_d and O_h surroundings are simultaneously implemented, e.g. $[Mn(L1)_3][MnBr_4].^{[25]}$ The red band of 5 has a mono-exponential decay with the lifetime being peculiar for Mn^{2+} -based phosphorescence, i.e. $\tau = 1.11$ ms.^[16-25]



Figure 11. Emission spectra of solid 5 recorded at the different excitations ($\lambda_{ex} = 250-300$ nm).

Conclusions

In summary, the reaction of Mn(NCS)₂ with diverse bis(phosphine oxide) ligands, Ph₂P(O)–X–(O)PPh₂, has been

systematically investigated and a series of molecular complexes and CPs thus has been synthesized. The structure of the bis(phosphine oxides) is demonstrated to play a decisive role in structure and dimensionality of the products formed. For example, ligands with spacers $X = "CH_2"$, "CH₂CH₂CH₂" or "CH₂C(=CH₂)CH₂", upon contact with Mn(NCS)2, afford bis-chelating complexes of $[Mn^{II}(O^O)_2(NCS)_2]$ kind. The reaction with the ligand bearing "C(=CH2)C(=CH2)" linker results in "two-in-one" complex $[Mn^{II}(O^{O})_{3}][Mn^{II}(NCS)_{4}]$, incorporating both tetrahedral and octahedral Mn²⁺ ions in a single structure. The acetylene-based phosphine oxide, Ph₂P(O)C≡C(O)PPh₂, reacts with Mn(NCS)₂ to assemble 1D chain coordination polymer [MnII(O^O)2(NCS)2]n, wherein octahedrally-coordinated metal ions are bridged by the ligands in a [Mn(0^0)Mn] fashion. Finally, Ph2P(O)CH2CH2(O)PPh2 under similar conditions (r.t., air, EtOH/acetone media) unexpectedly produces mixed-valent CP. $[Mn^{II}Mn^{III}(O^O)_3(NCS)_5]_n$, in which Mn^{II} and Mn^{III} centers are linked by the ligands into 1D chain. The photophysical study reveals a noticeable dual luminescence for [Mn^{II}(O^O)₂(NCS)₂] complexes Ph₂P(O)CH₂CH₂CH₂(O)PPh₂ basing on and Ph2P(O)CH2C(=CH2)CH2(O)PPh2 ligands. In the solid-state at room temperature both complexes manifest multicolor emission displayed by blue and red complementing bands, which are originated from intraligand fluorescence and Mn2+-centered phosphorescence, respectively. The relative ratio of these bands is effectively controlled by excitation wavelength that provides a powerful tool for fine-tuning the luminescence color from a deep-blue to a red. In general, the synthesized compounds, to our knowledge, are essentially first emissive Mn^{II} thiocyanate complexes. On a fundamental level, the findings presented contribute to coordination chemistry and photophysics of manganese compounds. From a practical viewpoint, the new results open up rich opportunities for design of stable and low-cost single molecule-based materials with tunable emission characteristics.

Experimental Section

Materials and Methods: The reactions were carried out under ambient conditions (23–25 °C, air). MnCl₂·4H₂O (\geq 99.0%, Aldrich), NaNCS (99.9%, Reactiv) and MeCN (HPLC grade, Cryochrom) were used as purchased. The ligands **L1–4**^[54] and **L5**^[55] were prepared following the published procedures. **L6** was synthesized by oxidation of the corresponding bis-phosphine (98%, Aldrich) in H₂O₂/H₂O/acetone system.

PXRD patterns were recorded on a Shimadzu XRD-7000 diffractometer (Cu-K α radiation, Ni – filter, 3–35° 2 θ range, 0.03° 2 θ step, 5s per point). FT-IR spectra were measured on a Bruker Vertex 80 spectrometer at ambient temperature. Thermogravimetric analyses (TGA/DTG/c-DTA) were conducted in a closed Al₂O₃ pan under argon flow at 10 °C/min⁻¹ heating rate using a NETZSCH STA 449 F1 Jupiter STA instrument.

Photophysical measurements: Photoluminescence and excitation luminescence spectra were recorded at room temperature using Fluorolog-3 (Horiba Jobin Yvon) equipped with a 450 W ozone-free Xe lamp, double grating excitation and emission monochromators. Emission and excitation spectra were corrected for source intensity (lamp and grating) and emission spectral response (detector and grating) by standard correction curves. The luminescence decays (Figures S8–10) were recorded on the same instrument.

 $Mn(SCN)_2$. To a solution of MnCl₂·4H₂O in EtOH, solution of NaSCN in acetone was added and the mixture was stirred at ambient temperature for 10 min. The precipitated NaCl was filtered-off and the freshly prepared Mn(SCN)₂ was then used for synthesis of **1–6**.

[$Mn^{II}(L1)_2(NCS)_2$]·2DMF (1·2DMF). To a solution of Mn(NCS)₂ (16 mg, 0.09 mmol) in EtOH/acetone (2 mL), L1 (60 mg, 0.14 mmol) was added. The mixture was stirred at ambient temperature for 1 h, and the precipitated powder of 1 was then dissolved in DMF (1 mL). Resulting solution was placed into a closed weighing bottle containing a diethyl ether on a bottom. After keeping for 24 h, colorless crystals formed were collected and dried on air. Yield: 35 mg (67%). FT-IR (KBr, cm⁻¹): 388 (m), 407 (w), 430 (m), 447 (w), 457 (w), 473 (w), 505 (vs), 519 (s), 569 (m), 615 (w), 660 (m), 679 (s), 692 (vs), 721 (s), 743 (vs), 756 (s), 787 (vs), 930 (w), 995 (m), 1028 (w), 1072 (m), 1092 (m), 1099 (m), 1123 (s), 1180 (vs), 1202 (s), 1258 (w), 1317 (w), 1339 (w), 1360 (w), 1389 (s), 1406 (w), 1439 (vs), 1483 (m), 1589 (m), 1661 (vs), 1973 (w), 2075 (vs), 2085 (vs). Anal. Calcd for Cs₈H₅₈MnN₄O₆P₄S₂ (1050.02): C, 60.6; H, 5.1; N, 4.9; S, 5.6. Found: C, 60.3; H, 4.9; N, 4.8; S, 5.5.

[*Mn^{III}*(*L2*)₃(*NCS*)₅]_n(2). To a solution of Mn(NCS)₂ (24 mg, 0.14 mmol) in EtOH/acetone (2 mL), **L2** (60 mg, 0.14 mmol) was added. The mixture was stirred at ambient temperature for 1 h, and a resulting colorless solution was then filtered. A vial with the filtrate then was placed into a closed weighing bottle containing a diethyl ether on a bottom. After keeping for 24 h, colorless crystals formed were collected and dried on air. Yield: 55 mg (47%). FT-IR (KBr, cm⁻¹): 420 (w), 478 (m), 500 (m), 511 (s), 534 (vs), 554 (s), 677 (m), 692 (s), 727 (vs), 750 (s), 762 (m), 997 (w), 1026 (w), 1070 (m), 1099 (s), 1123 (s), 1140 (m), 1163 (vs), 1180 (s), 1287 (w), 1314 (w), 1337 (w), 1369 (w), 1389 (w), 1408 (m), 1437 (s), 1483 (w), 1589 (w), 1655 (m), 1692 (w), 2039 (s), 2045 (s), 2068 (vs), 2085 (s). Anal. Calcd for C_{83H72}Mn₂N₅O₆P₆S₅ (1691.53): C, 58.9; H, 4.3; N, 4.1; S, 9.5. Found: C, 59.1; H, 4.3; N, 4.0; S, 9.2.

[*Mn^H*(*L3*)₂(*NCS*)₂] (*3*). To a solution of Mn(NCS)₂ (16 mg, 0.09 mmol) in EtOH/acetone (2 mL), *L3* (64 mg, 0.14 mmol) was added. The mixture was stirred at ambient temperature for 1 h, and the precipitated white powder of **3** was centrifuged and dried in vacuum. Yield: 30 mg (63%). FT-IR (KBr, cm⁻¹): 397 (w), 426 (w), 447 (w), 505 (s), 538 (s), 555 (s), 664 (m), 694 (vs), 723 (vs), 746 (s), 822 (w), 934 (w), 943 (w), 997 (w), 1028 (w), 1070 (w), 1103 (s), 1123 (s), 1171 (vs), 1329 (w), 1341 (w), 1350 (w), 1398 (m), 1437 (s), 1485 (w), 1591 (m), 2064 (vs), 2085 (vs). Anal. Calcd for C₅₆H₅₂MnN₂O₄P₄S₂ (1059.98): C, 63.4; H, 4.9; N, 2.6; S, 6.1. Found: C, 63.1; H, 4.7; N, 2.9; S, 6.5.

[$Mn^{II}(L4)_2(NCS)_2$] (4). To a solution of Mn(NCS)₂ (12 mg, 0.07 mmol) in EtOH/acetone (2 mL), L4 (60 mg, 0.13 mmol) was added. The mixture was stirred at ambient temperature for 1 h, and the precipitated white powder of 4 was centrifuged and dried in vacuum. Yield: 25 mg (66%). FT-IR (KBr, cm⁻¹): 409 (w), 432 (m), 463 (m), 469 (m), 503 (s), 513 (vs), 544 (s), 588 (vs), 692 (vs), 719 (vs), 748 (s), 777 (m), 789 (w), 833 (s), 858 (w), 868 (w), 920 (m), 995 (w), 1028 (w), 1074 (m), 1103 (s), 1123 (s), 1150 (s), 1179 (vs), 1231 (m), 1240 (m), 1283 (m), 1312 (w), 1321 (w), 1341 (w), 1383 (m), 1395 (m), 1439 (s), 1487 (w), 1593 (m), 1636 (m), 1703 (vw), 1815 (vw), 1834 (vw), 1892 (vw), 1910 (vw), 2079 (vs). Anal. Calcd for C₅₈H₅₂MnN₂O₄P4_{S2} (1083.95): C, 64.3; H, 4.8; N, 2.6; S, 5.9. Found: C, 64.0; H, 4.6; N, 2.6; S, 5.6.

 $[Mn^{II}(L5)_3][Mn^{II}(NCS)_4]$ (5). To a solution of Mn(NCS)₂ (16 mg, 0.09 mmol) in EtOH/acetone (2 mL), L5 (60 mg, 0.13 mmol) was added. The mixture was stirred at ambient temperature for 1 h, and the precipitated powder of 5 was centrifuged and dried in vacuum. Yield: 90 mg (58%). FT-IR (KBr, cm⁻¹): 428 (w), 465 (w), 480 (w), 505 (s), 538 (vs), 577 (s), 596 (s), 615 (w), 673 (m), 696 (vs), 729 (vs), 754 (s), 775 (m), 914 (w), 966 (m), 997 (w), 1026 (w), 1072 (m), 1101 (s), 1121 (s), 1179 (vs), 1207 (s), 1314 (w), 1383 (w), 1416 (m), 1437 (s), 1483 (m), 1589 (w), 1630 (w), 1722 (w), 2054 (vs). Anal. Calcd for C₈₈H₇₂Mn₂N₄O₆P₆S₄ (1705.43): C, 62.0; H, 4.2; N, 3.3; S, 7.5. Found: C, 62.1; H, 4.4; N, 3.3; S, 7.6.

 $[Mn^{H}(L6)_2(NCS)_2]_n$ (6). To a solution of Mn(NCS)₂ (16 mg, 0.09 mmol) in EtOH/acetone (2 mL), L6 (40 mg, 0.09 mmol) was added. The

mixture was stirred at ambient temperature for 1 h, and diethyl ether (8 mL) was added then to a resulting mixture. The precipitated powder was centrifuged and dried under vacuum. Yield: 63 mg (68%). FT-IR (KBr, cm⁻¹): 432 (w), 482 (w), 515 (s), 534 (vs), 584 (w), 619 (vw), 689 (s), 706 (m), 729 (s), 750 (m), 816 (vs), 997 (m), 1026 (w), 1070 (w), 1101 (m), 1124 (s), 1186 (vs), 1198 (s), 1314 (w), 1337 (vw), 1439 (vs), 1483 (w), 1574 (vw), 1589 (m), 2070 (vs). Anal. Calcd for C₅₄H₄₀MnN₂O₄P₄S₂ (1023.87): C, 63.3; H, 3.9; N, 2.7; S, 6.3. Found: C, 63.0; H, 3.9; N, 3.0; S, 6.5.

Supporting Information (see footnote on the first page of this article): CCDC 1963966–1963971 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center at http://www.ccdc.cam.ac.uk/data_request/cif.

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FULL PAPER

First representatives of luminescent Mn^{II} thiocyanate complexes were assembled reacting the $Mn(NCS)_2$ with diverse bis(phosphine oxides) ligands of $Ph_2P(O)-X-(O)PPh_2$ type. Some of such complexes feature an intriguing solid-state dual emission expressed by "blue" and "red" bands which are originated from intraligand fluorescence and Mn^{2+} -centered phosphorescence, respectively.



Dual luminescence

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Manganese(II) thiocyanate complexes with bis(phosphine oxide) ligands: synthesis and excitation wavelengthdependent multicolor luminescence