

Manganese(II), Iron(II), Cobalt(II) and Nickel(II) Complexes of Methanesulfonic Acid Hydrazide. Crystal Structure of *trans*-Dichlorotetrakis(methanesulfonic Acid Hydrazide-*N*²)cobalt(II) and *trans*-Dichlorotetrakis(methanesulfonic Acid Hydrazide-*N*²)nickel(II)

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Methanesulfonic Acid Hydrazide, Metal Complexes, X-Ray Structure

The complexes [M(MSH)₄Cl₂] (MSH = CH₃SO₂NHNH₂; M = Mn (**1**), Fe (**2**), Co (**3**) and Ni (**4**)) were synthesized and characterized by elemental analysis, molar electric conductivity, IR and *d-d* electronic spectra. The X-ray single crystal analysis revealed for **3** (triclinic, *P* $\bar{1}$, *a* = 8.077(2), *b* = 8.622(2), *c* = 8.742(2) Å, α = 71.98(3), β = 75.30(3), γ = 64.11(3)°, *V* = 515.8(2) Å³, *Z* = 1) and **4** (triclinic, *P* $\bar{1}$, *a* = 8.050(2), *b* = 8.588(2), *c* = 8.686(2) Å, α = 73.35(3), β = 75.76(3), γ = 63.94(3)°, *V* = 511.8(2) Å³, *Z* = 1) that MSH is coordinated *via* the amino N atom, the donor atoms and the metal are coplanar, and the Cl ligands are in *trans*-configuration. On the basis of IR data a similar structure is suggested for **1** and **2**. The electronic spectra of **3** and **4** are interpreted by the Angular Overlap Model and bonding parameters are derived: $e_{\sigma}(\text{N}) = 3384(15)$, $e_{\sigma}(\text{Cl}) = 2788(25)$, $e_{\pi}(\text{Cl}) = 150(21)$ cm⁻¹ for **3**, and $e_{\sigma}(\text{N}) = 3668(21)$, $e_{\sigma}(\text{Cl}) = 2602(150)$, $e_{\pi}(\text{Cl}) = -21(128)$ cm⁻¹ for **4**.

Introduction

Sulfonamide [1–3], and hydrazine [4] derivatives, as well as compounds containing both fragments in the same molecule [5] exhibit versatile pharmacological activity, and in particular, a cytostatic effect. Transition metal complexes of hydrazides and sulfonamides also find application in chemotherapy [6]. Complexes of aromatic sulfonamides and sulfonylhydrazines have been intensively studied as carbonic anhydrase inhibitors [7].

Methanesulfonic acid hydrazide (MSH), CH₃SO₂NHNH₂, is the prototype of the compounds combining the two pharmacophoric groups, sulfonamide and hydrazine residue. Previously we studied the crystal structure and vibrational spectra of MSH [8], and synthesized and characterized its azomethine derivatives [9, 10]. The parent compound and its azomethine derivatives exhibit antibacterial and cytostatic activity [9]. MSH is apparently a potential ligand, and its metal complexes could also be of interest for pharmacology. However, the coordination chemistry of MSH has not been explored. Recently we reported [11] the preparation and X-ray crystal

structure analysis of [Zn(MSH)₂Cl₂], which revealed that the coordination of zinc is pseudo-tetrahedral and the ligand is bound to it *via* the NH₂ group.

Here we report the synthesis, spectroscopic and structural characterization of Mn(II), Fe(II), Co(II), and Ni(II) complexes of MSH.

Results and Discussion

The new complexes, all of the type [M(MSH)₄Cl₂], were prepared from MSH and metal chlorides in organic solvents (see Experimental). Analytical results and some physical properties of the compounds are listed in Table 1. The complex **1** is hygroscopic and should be handled and stored in a dry atmosphere. On exposure to air, **2** slowly turns to yellow, because of oxidation to Fe(III), and should be stored in a sealed ampule. Compounds **3** and **4** are stable under usual conditions. All the complexes are soluble in water, methanol and ethanol; **1**, **2** and **3** are also soluble in acetonitrile, and **1** in tetrahydrofuran.

The attempts to isolate Pd(II) and Pt(II) complexes of MSH were unsuccessful. Upon mixing

Table 1. Elemental analyses and physical properties of MSH complexes.

No.	Complex Formula	C	Analysis: found (calcd) [%]				Metal	Colour	Melting range ^a [°C]	$\Lambda_m^b, \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$	
			H	N	O	S				MeOH	EtOH
1	[Mn(MSH) ₄ Cl ₂]	8.78 (8.48)	4.85 (4.27)	19.89 (19.79)	22.64 (22.60)	23.18 (22.64)	10.20 (9.70)	white	98–100	115	29
2	[Fe(MSH) ₄ Cl ₂]	8.70 (8.47)	4.44 (4.26)	19.15 (19.75)	22.86 (22.56)	22.21 (22.61)	10.22 (9.85)	yellow- ish-white	137–139	130	37
3	[Co(MSH) ₄ Cl ₂]	8.68 (8.42)	4.31 (4.24)	19.51 (19.65)	22.10 (22.44)	22.74 (22.48)	10.61 (10.33)	pink	157–160	115	27
4	[Ni(MSH) ₄ Cl ₂]	8.97 (8.43)	4.81 (4.24)	19.27 (19.65)	22.96 (22.45)	22.23 (22.49)	10.44 (10.29)	sky-blue	186–190	112	33

^a With decomposition; ^b molar electric conductivity of 1×10^{-3} M solutions of the complexes in methanol and ethanol.

water solutions of MSH, and of K₂PdCl₄, K₂PtCl₄ and K₂PtI₄, respectively, yellow precipitates are formed initially, which rapidly decompose at ambient temperature. The ligand is oxidized with release of gaseous product, probably N₂, and deposition of metallic Pd and Pt, respectively. Oxidation of MSH was also observed by Fe(III), Cu(II), and Ag(I) salts.

The molar electric conductivity (Λ_m) values of the complexes (Table 1) are much higher than the expected for non-electrolytes, and reach the ranges characteristic for the 1:1 electrolyte type, in both methanol and ethanol [12]. This shows that partial dissociation of the chloride ligands takes place in these solvents.

Crystal structure of **3** and **4**

Although the crystal structure of metal coordination compounds of hydrazine and its derivatives has been extensively studied by Braibanti *et al.* [13], and by other workers [14–16], it seems that there are few examples of structurally characterized coordinated sulfonylhydrazines [11, 17].

Complexes **3** and **4** are isostructural; the molecular structure of **3** is presented in Fig. 1. Selected geometric parameters for **3** and **4** are listed in Table 2. The ligand MSH is bound to the metal atom by the NH₂ groups. The sulfonyl oxygens do not participate in the coordination, and this is not surprising since the examples of coordinated sulfonyl groups are very rare [18]. The four N donor

Parameter	3 , M = Co		4 , M = Ni	
	n = 1	n = 2	n = 1	n = 2
M–Cl	2.425(1)		2.447(1)	
M–N(n2)	2.186(2)	2.177(2)	2.122(2)	2.123(2)
S(n)–O(n1)	1.435(1)	1.438(1)	1.442(2)	1.440(2)
S(n)–O(n2)	1.440(1)	1.443(1)	1.462(2)	1.462(2)
S(n)–N(n1)	1.665(2)	1.659(2)	1.657(2)	1.655(2)
S(n)–C(n)	1.756(2)	1.752(2)	1.758(2)	1.751(2)
N(n1)–N(n2)	1.436(2)	1.434(2)	1.445(2)	1.440(2)
Cl–M–N(n2)	89.32(5)	89.34(5)	89.06(6)	88.74(5)
N(12)–M–N(22)	91.85(6)		91.32(7)	
N(n1)–N(n2)–M	110.8(1)	109.8(1)	110.4(1)	109.9(1)
O(n1)–S(n)–O(n2)	118.7(1)	118.7(1)	119.0(1)	119.1(1)
O(n1)–S(n)–N(n1)	110.7(1)	110.5(1)	110.6(1)	110.7(1)
O(n2)–S(n)–N(n1)	104.8(1)	104.3(1)	104.7(1)	104.1(1)
O(n1)–S(n)–C(n)	108.8(1)	108.8(1)	108.4(1)	107.9(1)
O(n2)–S(n)–C(n)	109.6(1)	109.8(1)	110.1(1)	110.6(1)
N(n2)–N(n1)–S(n)	116.6(1)	117.9(1)	116.4(1)	118.0(1)
N(n1)–S(n)–C(n)	103.1(1)	103.6(1)	102.8(1)	103.3(1)
N(n2)–N(n1)–S(n)–C(n)	–93.6(1)	95.9(1)	–92.7(2)	94.4(2)
H(n4)–N(n1)–S(n)–C(n)	144(2)	–137(2)	144(2)	–137(2)
H(n5)–N(n2)–N(n1)–H(n4)	82(3)	–84(3)	79(3)	–83(3)
H(n6)–N(n2)–N(n1)–H(n4)	–163(3)	158(3)	–162(3)	162(3)

Table 2. Selected bond lengths (Å) and angles (deg) for complexes **3** and **4**. Atom labelling according to Fig. 1.

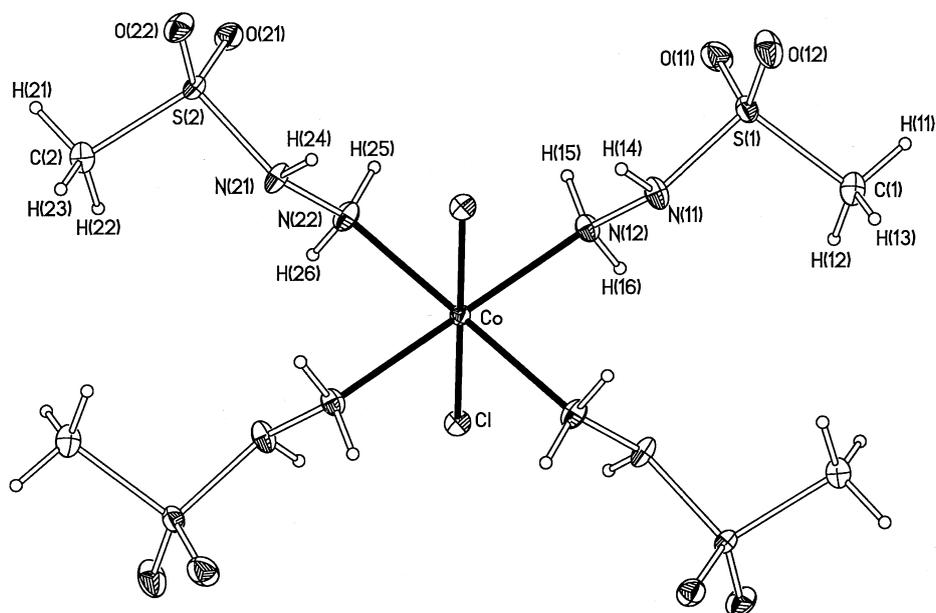


Fig. 1. ORTEP drawing for $[\text{Co}(\text{MSH})_4\text{Cl}_2]$ (**3**). Ellipsoids are at the 50% probability level.

atoms and the metal are coplanar and the two Cl ligands are in *trans*-position to each other. The coordination polyhedron MN_4Cl_2 approaches almost D_{4h} symmetry. The M–N bond lengths in **3** and **4** have the usual values for a coordinated hydrazine group [13]. The Co–N bonds are longer (average by *ca.* 0.06 Å) as compared to the Ni–N bonds, whereas the Co–Cl bonds are somewhat shorter (by *ca.* 0.02 Å) with respect to the Ni–Cl bonds. Thus the tetragonal deformation is more pronounced in **4** than in **3**. The symmetry of the complex molecule is near to C_{2h} , although the true point group is C_i .

It is interesting to compare the conformation of the ligand in **3** and **4**, with that in $[\text{Zn}(\text{MSH})_2\text{Cl}_2]$ [11], as well as in the non-coordinated MSH where in the solid state two molecules of MSH dimerize through hydrogen bonds between the NH_2 and NH groups [8]. In the Zn(II) complex the sulfonamide nitrogen is completely planarized, in distinct with the MSH dimer where the sum of the bond angles at this atom is 347°. In **3** and **4** the sulfonamide nitrogen is less planarized as evidenced by the sum of the bond angles (334–339°). The conformations of MSH with respect to the rotation around the S–N bond differ signifi-

cantly in the three cases. In the Zn(II) complex, the amino group is in *gauche*-orientation with respect to S–C and one of the S–O bonds, and the hydrogen atom at the sulfonamide nitrogen and the other oxygen are almost eclipsed. In the dimer of the MSH, both the NH_2 group and the H atom at the sulfonamide nitrogen are *gauche*-oriented with respect to the S–C and S–O bonds. In complexes **3** and **4**, however, the NH_2 group is *gauche*-oriented toward the S–C and S–O bonds, but the H atom is *gauche*-positioned toward the two S–O bonds. The bond lengths and bond angles do not vary considerably in the three regarded cases.

Fig. 2 shows the crystal packing and hydrogen bonding geometry for **3**; for **4** they are analogous. The parameters of the hydrogen bonds for **3** and **4** are collected in Table 3. All types of hydrogen atoms, even those of the methyl groups (one H atom *per* CH_3 group), are involved in a system of hydrogen bonds. The hydrogen atom of the NH groups has short contacts with the Cl ligands, and those of the NH_2 groups with the sulfonyl oxygen atoms. The NH groups participate in intramolecular hydrogen bonds, whereas the NH_2 and CH_3 groups are involved in both intra- and intermolecular bonds.

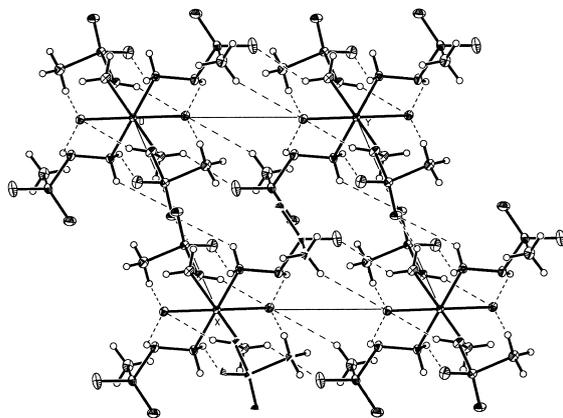


Fig. 2. The crystal packing of $[\text{Co}(\text{MSH})_4\text{Cl}_2]$ (**3**). Hydrogen bonds are indicated by dashed lines.

Infrared spectra

Previously, [8] an entire interpretation of the vibrational spectra of MSH, supported by normal coordinate analysis, has been done which helped the full assignment of IR bands of the coordinated MSH. The assignments are based on the literature data for molecules containing appropriate fragments, a sulfonyl group [19–22] and a hydrazine residue [23, 24] (an expanded reference list can be found in [8]), as well as for metal complexes of hydrazine derivatives [11, 25–29], including sulfonylhydrazines [7c, d]. There is a close correspondence between the spectra of the four coordination compounds studied which suggest all they should be of the same structural type. Selected IR spectroscopic data for MSH and its complexes are presented in Table 4. For better assignment of the bands of the hydrazine residue, and in particular, the wagging, twisting and rocking modes of the

NH_2 group, the spectrum of partially deuterated specimen of complex **4** was examined (Fig. 3, Table 4). An alternative assignment concerning the NH_2 rocking vibrations could not be ruled out, the bands in the interval of $585\text{--}623\text{ cm}^{-1}$ to be ascribed to them. In such a case the band at 470 cm^{-1} in the spectrum of the deuterated complex **4** would correspond to that at 623 cm^{-1} for the non-deuterated complex (isotopic ratio 1.33). If this is so, all the three bands in the range of $490\text{--}535\text{ cm}^{-1}$ should be attributed to SO_2 bending vibrations.

Among the five IR-active normal vibrations of the D_{4h} coordination polyhedron MN_4Cl_2 , [30] we could tentatively point out the A_{2u} metal-chlorine stretching, ascribing to it the bands in the interval of $243\text{--}255\text{ cm}^{-1}$ (Table 4). These are the most intensive bands in the far IR region and their position conforms with the data for complexes with relevant structure [30–33].

d-d Electronic spectra

The Angular Overlap Model (AOM) is an appropriate tool for interpreting *d-d* electronic spectra of complexes with symmetry lower than cubic, and has been successfully applied to tetragonal complexes with the MN_4Hal_2 chromophores [30, 34, 35]. Fig. 4 shows the diffuse-reflectance electronic spectra of **3** and **4**, along with the assignment of the *d-d* transitions. The bands in the range of $5900\text{--}6700\text{ cm}^{-1}$, and the shoulders at 7350 cm^{-1} appear in the spectra of all the four complexes and should be ascribed to overtone and combination vibrational transitions of the ligand. The *d-d* spectra of **3** and **4** were analysed by AOM (D_{4h} symmetry of the

Table 3. Hydrogen bonding geometry for complexes **3** and **4**^a.

DH...A	D–H, Å		H...A, Å		D...A, Å		< (DHA), deg	
	3	4	3	4	3	4	3	4
N(21)H(24)...Cl ⁽ⁱ⁾	0.86(2)	0.83(3)	2.39(2)	2.41(3)	3.105(2)	3.080(2)	140(2)	138(2)
N(22)H(25)...O(21) ⁽ⁱⁱ⁾	0.89(2)	0.86(3)	2.39(2)	2.43(3)	3.060(2)	3.051(2)	132(2)	130(3)
N(22)H(26)...O(12) ⁽ⁱⁱⁱ⁾	0.85(2)	0.87(3)	2.35(2)	2.34(3)	3.009(2)	3.040(2)	135(2)	138(2)
N(12)H(16)...O(22) ^(iv)	0.84(2)	0.86(3)	2.31(2)	2.34(3)	3.041(2)	3.071(2)	146(2)	143(2)
N(12)H(15)...O(21) ⁽ⁱⁱ⁾	0.91(2)	0.91(3)	2.49(2)	2.52(3)	3.178(2)	3.190(2)	133(2)	131(2)
N(11)H(14)...Cl ⁽ⁱ⁾	0.81(2)	0.85(3)	2.45(2)	2.39(3)	3.114(2)	3.066(2)	140(2)	137(2)
C(1)H(13)...Cl ^(v)	0.95(3)	0.91(4)	2.81(3)	2.86(4)	3.698(2)	3.702(2)	156(2)	154(3)
C(2)H(23)...Cl ^(vi)	0.96(2)	0.95(3)	2.76(2)	2.75(3)	3.573(2)	3.569(2)	142(2)	145(2)

^a Symmetry transformations used to generate equivalent atoms: ⁽ⁱ⁾ $-x, -y, -z$; ⁽ⁱⁱ⁾ $-x + 1, -y, -z$; ⁽ⁱⁱⁱ⁾ $x, y + 1, z$; ^(iv) $x, y, z - 1$; ^(v) $x, y - 1, z$; ^(vi) $x, y, z + 1$.

Table 4. Selected IR bands ($\bar{\nu}$, cm^{-1}) for MSH and its complexes in CsI.

MSH	1	2	Compound No.			Assignment
			3	4	4-deuterated	
3354sh ^a 3317 m	3323 m	3322 m	3320 m	3316 m	2479 m (1.34) ^b	$\nu_a(\text{NH}_2)^c$,
3277 m	3262 m	3266 m	3262 m	3259 m	2450w (1.33)	$\nu(\text{NH})$
3136 m	3220sh 3195 m	3228sh 3202 m	3228sh 3190 m 3181 m	3220sh 3184sh 3168 m	2406w (1.34) 2368 m (1.34)	$\nu_s(\text{NH}_2)$
1617 m	1620 m 1607sh	1620 m 1610sh	1619 m 1607sh	1619 m 1605sh	1192 m (1.36)	$\delta(\text{NH}_2)$
1395sh	1434sh	1433sh	1434sh	1435 m	1082 m (1.33)	$\delta(\text{NH})$
1335s	1334s	1336s	1336s	1339s	1332s (1.01)	$\delta_s(\text{CH}_3)$,
1318s	1317sh					$\nu_a(\text{SO}_2)$
1295sh	1202 m 1170sh	1207 m 1187 m	1212 m 1189 m	1217 m 1195 m	892w (1.36) 882sh (1.35)	$\tau(\text{NH}_2)$
1158s	1141s	1142s	1142s	1143s	1151s (0.99)	$\nu_s(\text{SO}_2)$
1130sh	1020sh 1005w	1020sh 1009w	1027sh 1016w	1032sh 1022w	1035w (1.00)	$\nu(\text{NN})$
937 m	1273 m	1272 m	1272 m	1274 m	1082 m (1.18)	$\omega(\text{NH}_2)$
850 m	905 m	907 m	909 m	912 m	850 m (1.07)	$\nu(\text{SN})$
764 m	756 m 744 m	756 m 746 m	757 m 746 m	758 m 747 m	730w (1.04) 719w (1.04)	$\nu(\text{CS})$
650 m	625 m 585 m	627 m 598 m	642sh 611 m	657sh 623 m	558 m (1.18)	$\delta(\text{NH})$
529s	527 m	529 m	532 m	535 m	528 m (1.01)	$\delta(\text{SO}_2)$
–	510sh 490 m	510 m 494 m	510 m 498 m	512 m 501 m	443 m (1.14)	$\rho(\text{NH}_2)^d$
445 m	454 m	456 m	458 m	461 m	470 m (0.98)	$\omega(\text{SO}_2)$
409w	391w	396w	397w	397w	395w (1.01)	$\rho(\text{SO}_2)$
344 m	340w	341w	342w	345w	345w (1.00)	$\tau(\text{SO}_2)$
–	255 m	254 m	244 m	243 m	243 m (1.00)	$\nu(\text{MCl}_2)$, A_{2u}

^a Abbreviations: m – medium, s – strong, sh – shoulder, w – weak; ^b isotopic ratio, $\bar{\nu}_H/\bar{\nu}_D$, in parentheses; ^c notations: a – asymmetric, s – symmetric, δ – bending, ν – stretching, ρ – rocking, τ – twisting, ω – wagging; ^d see the text for another possible assignment of $\rho(\text{NH}_2)$ modes.

MN_4Cl_2 chromophore) with fitting the calculated to the experimental wave numbers [36]. The parameters are presented in Table 5. The e_π parameters of the nitrogen ligands were assumed equal to zero [34] in these calculations. For **4**, the number of bands permitted all the three AOM parameters plus the Rakah B and C parameters to be optimized, and only the spin-orbit coupling parameter ζ was fixed to 550 cm^{-1} ($0.87 \zeta_{\text{Ni(II)}}(\text{free ion})$) [37]. The ratio between the optimized values of C and B is 3.84. In the case of **3**, fixed values were used for both C and ζ ; C was taken equal to 3.84 B (like for **4**), and ζ was assumed 450 cm^{-1} [38]. The McClure parameters $d\sigma$ and $d\pi$ [39a] derived for **3** are -447 and 150 cm^{-1} , respectively; and for **4** they are -799 and -21 cm^{-1} , respectively. As evidenced by the AOM and McClure parameters, the tetragonal deformation in complexes **3** and **4** is relatively weak with respect to other complexes with

trans- $[\text{MN}_4\text{Cl}_2]$ ($M = \text{Co}, \text{Ni}$) chromophores [30, 34, 40] and is more pronounced for the Ni(II) complex as compared to the Co(II) analogue. The data of Lever *et al.* [34b, c] on such complexes with *sym*-diethylethylenediamine show that $d\sigma$ parameter (negative) is larger in absolute value for the Ni(II) complex than for the Co(II) one. The values of the e_σ parameters of **3** and **4**, which are a measure of the tetragonal deformation (the e_π parameters are small), correlate with the $M-N$ and $M-Cl$ bond lengths (Table 2): the $\text{Ni}-N$ bonds are shorter than $\text{Co}-N$, and the $\text{Ni}-Cl$ bonds are longer than $\text{Co}-Cl$. The values of the average splitting parameter Dq_{ave} [39a] for **3** and **4** are 936 and 997 cm^{-1} , respectively.

The diffuse reflectance spectrum of complex **2** exhibits a broad band with a maximum at *ca.* 10000 cm^{-1} . This band is poorly resolved and no conclusions regarding the tetragonal deformation

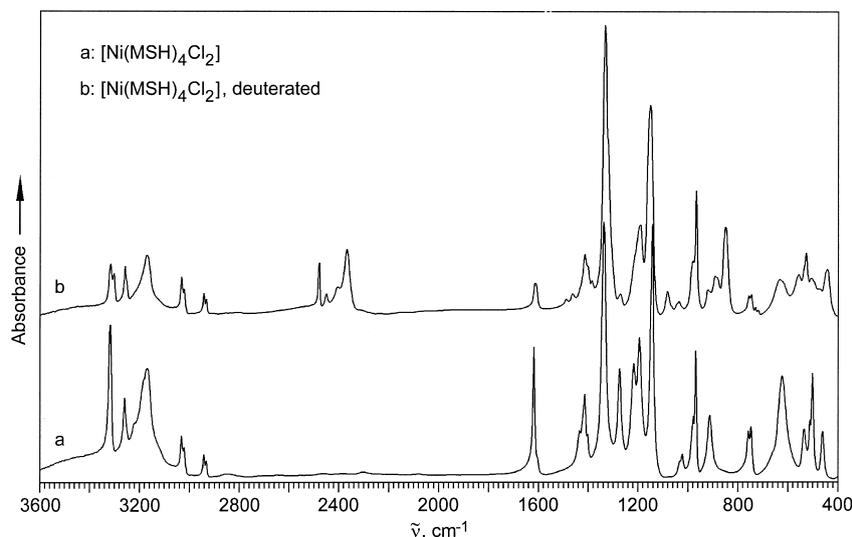


Fig. 3. IR spectra of non-deuterated and partially deuterated $[\text{Ni}(\text{MSH})_4\text{Cl}_2]$ (**4**) in CsI disks.

Table 5. AOM parameters^a (cm^{-1}) for complexes **3** and **4**.

Parameter	3	4
$e_\sigma(\text{N})$	3384(15) ^b	3668(21)
$e_{\pi c}(\text{N}), e_{\pi s}(\text{N})$	0 ^c	0 ^c
$e_\sigma(\text{Cl})$	2788(25)	2602(150)
$e_{\pi c}(\text{Cl}), e_{\pi s}(\text{Cl})$	150(21)	-21(128)
B	802(2)	832(5)
C	3079 ^c	3197(31)
ζ	450 ^c	550 ^c

^a For definition of the parameters see [39]; ^b standard deviations in parentheses; ^c fixed values are used in calculations.

could be done. The position of the band corresponds to the only spin-allowed transition ${}^5T_{2g} \rightarrow {}^5E_g$ in high-spin Fe(II) complexes with effective octahedral symmetry, and gives the value of the averaged $10 Dq_{\text{ave}}$ parameter [39a], which is similar to that of complexes **3** and **4**.

It is known [39a] that $d-d$ bands of hexacoordinated high-spin Mn(II) complexes have extremely low intensity and in the presence of organic ligands they could rarely be detected. This is also the case with complex **1**. Nevertheless, the two weak absorptions observed in the diffuse reflectance spectrum of **1**, at *ca.* 15700 and 24100 cm^{-1} , could tentatively be ascribed to the transitions ${}^6A_{1g} \rightarrow {}^4T_{1g}$ and ${}^6A_{1g} \rightarrow {}^4A_{1g}, {}^4E_g(G)$, respectively [39a].

Experimental

Starting compounds

Hydrated metal chlorides and other chemicals were commercial products (*purum* or *pro analysi*). When necessary, metal chlorides were dehydrated with 2,2-dimethoxypropane [41] and the solvents were purified by the routine procedures [42]. MSH was prepared by the procedure of Powell and Whiting [43], with some modifications [8].

Preparation of the complexes

$[\text{Mn}(\text{MSH})_4\text{Cl}_2]$ (**1**). 0.25 g (1.99 mmol) of MnCl_2 was dissolved in a mixture of ethanol and acetonitrile (0.5 and 1.2 ml, respectively), and a solution of 0.91 g (8.26 mmol) of MSH in acetonitrile (2 ml) was added. The reaction mixture was heated at 40 °C for 10 min, then it was cooled to room temperature, diethyl ether (1 ml) was added and the solution was left in a freezer at -30 °C overnight. The hygroscopic colourless crystals were filtered, washed with acetonitrile–diethyl ether mixture (1:1, 10 ml), then with diethyl ether and petroleum ether. These manipulations were carried out avoiding the access of moisture (CaCl_2 tube). The product was dried *in vacuo* over P_2O_5 . Yield: 0.41 g (36%). Because of hygroscopicity the compound was stored in a glass ampule.

$[\text{Fe}(\text{MSH})_4\text{Cl}_2]$ (**2**). 0.25 g (1.26 mmol) of freshly recrystallized ($\text{H}_2\text{O}/\text{HCl}$) $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ was dissolved in methanol (2.5 ml) under a layer of petroleum ether (to prevent the oxidation by air). The methanol used was previously deaerated by boil-

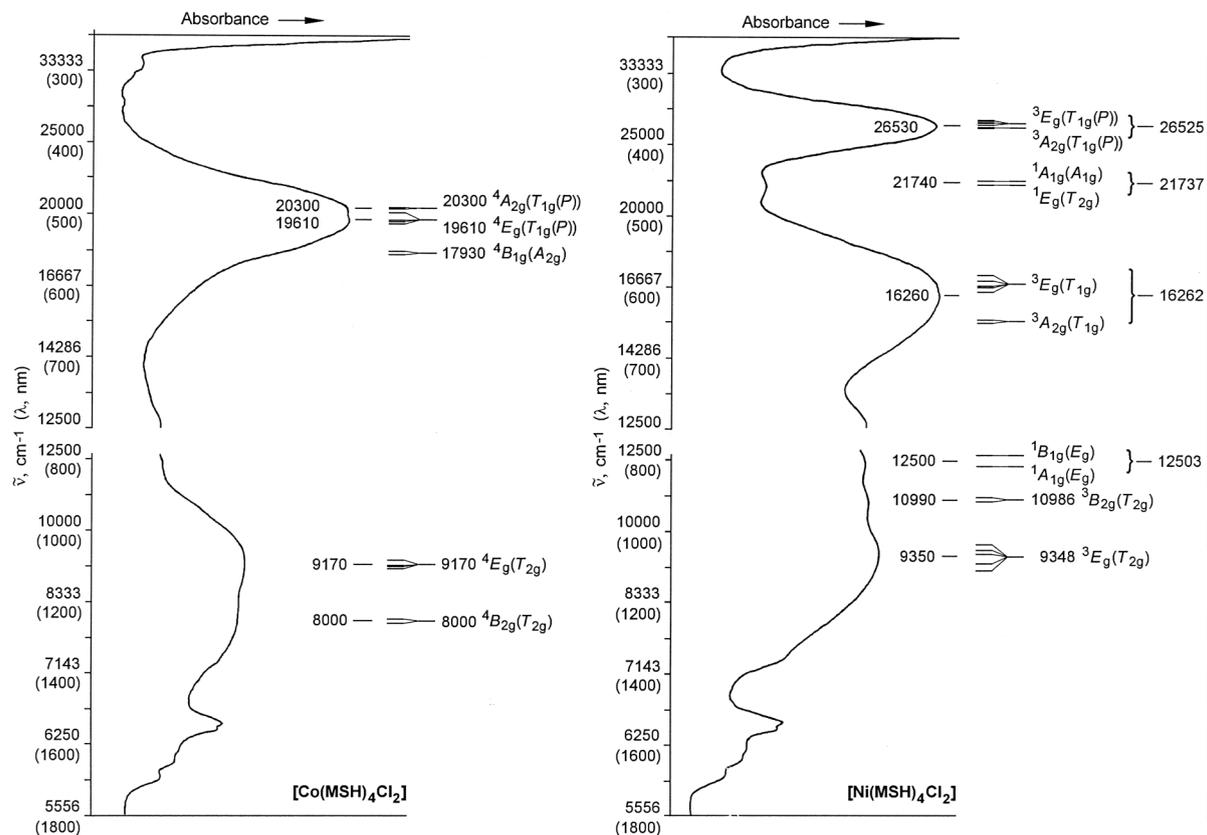


Fig. 4. Diffuse reflectance spectra of [Co(MSH)₄Cl₂] (**3**) and [Ni(MSH)₄Cl₂] (**4**) with assignments of *d-d* electronic transitions in *D*_{4h} MN₄Cl₂ chromophores. The schemes show the correlation between the experimental band maxima and the AOM calculated wave numbers (cm⁻¹) of the transitions, the symmetry of the excited states in *D*_{4h} and in *O*_h (in parentheses) and the spin-orbit splitting. The ground states are $^4E_g(T_{1g})$ for [Co(MSH)₄Cl₂], and $^3B_{1g}(A_{2g})$ for [Ni(MSH)₄Cl₂]; their energies are taken as zero. The AOM parameters are given in Table 5.

ing. The solution of FeCl₂·4H₂O was mixed with a solution of 0.57 g (5.18 mmol) of MSH in methanol (2.5 ml), the reaction mixture was heated at 40 °C for 5 min and left in a freezer at -30 °C for 2 h. The off-white crystalline precipitate was filtered and washed with diethyl ether (peroxide-free) under nitrogen. Yield: 0.48 g (67%). For recrystallization, the crude product was dissolved in hot deaerated methanol (7 ml) under a layer of petroleum ether. The solution was filtered and diethyl ether (2 ml) and petroleum ether (2 ml) were added. The solution was left at -30 °C overnight and the crystals – white, with a slight yellow tan – were filtered, washed with diethyl ether and petroleum ether under nitrogen. The product was dried *in vacuo* over P₂O₅. Yield of recrystallized complex: 0.25 g (52% of the crude product). To prevent the oxidation on air, the compound was stored in a glass ampule.

[Co(MSH)₄Cl₂] (**3**). A solution of 0.25 g (1.93 mmol) of CoCl₂ in methanol (2.5 ml) was mixed with a solution of 0.89 g (8.08 mmol) of MSH in the same solvent (4 ml). The mixture was heated at 40 °C for 5 min and left in an ice bath for 3 h. The pink crystals were filtered and washed with methanol (1 ml) and diethyl ether. Yield: 0.72 g (65%). The product was recrystallized from boiling methanol (16 ml). The crystals were filtered, washed with methanol – diethyl ether (1:3, 4 ml) and dried as above. Yield: 0.57 g (79% of the crude product). Crystal specimens suitable for X-ray diffraction analysis were obtained as follows. **3** (*ca.* 0.05 g) was dissolved in boiling methanol (1 ml), the solution was filtered and the filter washed with methanol (0.5 ml). This solution was carefully layered over carbon tetrachloride (*ca.* 5 ml) poured into a short tube. The tube was stoppered without shaking and left in a refrigerator

(0 °C). The two-layer system thus formed slowly homogenizes upon standing. After two weeks the pink crystals deposited were collected on a filter, washed and dried as above.

[Ni(MSH)₄Cl₂] (**4**). A solution of 0.25 g (1.93 mmol) of NiCl₂ in methanol (3 ml) was mixed with a solution of 0.89 g (8.08 mmol) of MSH in the same solvent (4 ml) and it was proceeded as above. Yield: 0.75 g (68%). The sky-blue product was recrystallized from boiling methanol (50 ml) and the crystals were filtered, washed and dried as above. Yield: 0.62 g (83% of the crude product). Crystals suitable for X-ray diffraction analysis were prepared by dissolving **4** (*ca.* 0.05 g) in boiling methanol (2.5 ml) and then proceeding as described for **3**. A partially deuterated specimen was prepared by dissolving **4** (*ca.* 0.015 g) in boiling methanol-d₄ (1.5 ml) and evaporation of the solvent *in vacuo*. The residue was treated in this way further 3 times. Finally the product was dried *in vacuo* over P₂O₅.

X-ray crystallography

The crystals of **3** and **4** (*vide supra*) were mounted on glass fiber and then flash-frozen to 100 K (Oxford Cryosystem-Cryostream Cooler). Preliminary examination and intensity data collections were carried out on a Kuma KM4 CCD α -axis diffracto-

meter with graphite-monochromated Mo-K α radiation. Crystals were positioned at 65 mm from the KM4CCD camera. 612 Frames were measured at 0.75° intervals with a counting time of 20 sec. The data were corrected for Lorentz and polarization effects. No absorption corrections were performed for the intensity data. Data reduction and analysis were carried out with the Kuma Diffraction (Wrocław) programs. The structure was solved by direct methods [44] (programme SHELXS97) and refined by the full-matrix least-squares method on all F^2 data using the SHELXL97 programmes [45]. All hydrogen atoms were found in a ΔF map. Crystal data and the details of data collection and the refinement procedure are collected in Table 6*.

Analyses, spectra and calculations

Melting points (uncorrected) were determined with a Boetius heating-plate microscope; the hygroscopic complex **1** being in a sealed capillary.

* Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre, CCDC-185160 and CCDC-185161. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code +(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk.

Table 6. Experimental data for the X-ray diffraction studies of complexes **3** and **4**.

Item	3	4
Empirical formula	C ₄ H ₂₄ Cl ₂ N ₈ CoO ₈ S ₄	C ₄ H ₂₄ Cl ₂ N ₈ NiO ₈ S ₄
<i>M</i>	570.38	570.16
Crystal system	triclinic	triclinic
Space group symbol	<i>P</i> 1̄	<i>P</i> 1̄
<i>a</i> [Å]	8.077(2)	8.050(2)
<i>b</i> [Å]	8.622(2)	8.588(2)
<i>c</i> [Å]	8.742(2)	8.686(2)
α [deg]	71.98(3)	73.35(3)
β [deg]	75.30(3)	75.76(3)
γ [deg]	64.11(3)	63.94(3)
<i>V</i> [Å ³]	515.8(2)	511.8(2)
<i>T</i> [K]	100(1)	100(1)
<i>Z</i>	1	1
Calculated density [Mg m ⁻³]	1.836	1.850
μ [mm ⁻¹]	1.546	1.667
Crystal dimensions [mm]	0.1 × 0.1 × 0.1	0.1 × 0.1 × 0.1
θ Range [deg]	3.49 to 28.27	4.02 to 28.30
Limiting indices	-6 ≤ <i>h</i> ≤ 10, -11 ≤ <i>k</i> ≤ 11, -11 ≤ <i>l</i> ≤ 11	-10 ≤ <i>h</i> ≤ 7, -11 ≤ <i>k</i> ≤ 10, -11 ≤ <i>l</i> ≤ 11
Number of reflections measured	3579	3493
Number of independent reflections	2272	2236
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0227 ^a , <i>wR</i> ₂ = 0.0571 ^b	<i>R</i> ₁ = 0.0367 ^a , <i>wR</i> ₂ = 0.0966 ^b
<i>R</i> Indices (all data)	<i>R</i> ₁ = 0.0261 ^a , <i>wR</i> ₂ = 0.0589 ^b	<i>R</i> ₁ = 0.0374 ^a , <i>wR</i> ₂ = 0.0976 ^b

^a $R(F) = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; ^b $wR_2 = \{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]\}^{1/2}$.

Electric conductivities were measured at 25 °C in methanol ($\lambda = 2.1 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$) and ethanol ($\lambda = 5.8 \times 10^{-7} \Omega^{-1} \text{ cm}^{-1}$) using a Hydromat conductivity meter. – The elemental analyses were performed according to standard microanalytical procedures; the metal content was determined by atomic absorption spectrometry (TÜBİTAK Laboratories, Ankara, Turkey). – Infrared spectra (4000–150 cm^{-1}) were recorded in the solid state as CsI and KBr disks and as nujol mulls on a Bruker IFS 113 spectrophotometer. The different modes of sampling gave practically identical spectra. – The diffuse reflectance electronic spectra (250–2000 nm) were taken on a Beckman

5270 spectrophotometer using BaSO_4 as a reference. – All spectral measurements were performed at room temperature. All sampling manipulations with the hygroscopic complex **1** were carried out in a dry box.

The electronic spectra were interpreted by means of the Angular Overlap Model [39] using the AOMX programme of Adamsky [36].

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