

Pyridine *N*-oxide and Quinoline *N*-oxide Complexes with Bivalent Manganese, Cobalt, Nickel, Copper, and Zinc Thiocyanates and Selenocyanates

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Pyridine *N*-oxide (pyo) and quinoline *N*-oxide (qno) form a variety of complexes with $[M(NCX)_2]$ acceptors ($M = Mn, Co, Ni, Cu, \text{ or } Zn; X = S \text{ or } Se$). Most of the complexes contain octahedrally co-ordinated metal ions; among the structural types identified are monomers {e.g., $[Co(pyO)_4(NCS)_2]$ }, pseudohalide-bridged species {e.g., $[Co(pyO)_2(NCS)_2]$ }, ligand-bridged species {e.g., $[Ni(qno)_2(NCS)_2]$ }, and ionic complexes {e.g., $[Mn(qno)_6] - [Mn(NCSe)_4]$ }. Many of the pyridine *N*-oxide complexes contain co-ordinated water or ethanol, but the quinoline *N*-oxide complexes do not. Assignments of the metal-ligand vibrations are discussed and compared with those for analogous pyridine complexes.

HETEROCYCLIC amine *N*-oxides are versatile ligands and react with transition-metal halides to form a variety of complexes,¹⁻⁴ not all of which have been fully characterised. We have prepared a series of complexes of pyridine *N*-oxide (pyo) and quinoline *N*-oxide (qno) with some transition-metal thiocyanate and selenocyanate acceptors, in the hope of obtaining additional structural information from the i.r. spectra of the co-ordinated pseudohalide anions.⁵

coupled with other vibrations of the ligand molecule.^{6,7} The pseudo-halide C-X stretching and NCX bending frequency regions are obscured by ligand absorptions in the spectra of many of the complexes.

$[Co(pyO)_4(NCS)_2]$, $[M(pyO)_3(NCX)_2 \cdot H_2O]$ ($M = Mn, Co, \text{ or } Ni; X = S \text{ or } Se$); $[M(pyO)_2(NCS)_2 \cdot EtOH]$ ($M = Co \text{ or } Ni$).—All these complexes have C-N stretching frequencies in the region (2 050—2 100 cm^{-1}) generally associated with the terminal *N*-bonded pseudohalide,⁵ and the visible spectra are consistent with octahedral co-ordination of the

TABLE I
Analytical data (%) and m.p.s

Complex	Found				Calc.				M.p. ($t/^\circ C$)
	C	H	NCX	M	C	H	NCX	M	
$[Co(pyO)_4(NCS)_2]$	46.5	3.5	20.7	10.5	47.5	3.6	20.9	10.6	130
$[Mn(pyO)_3(NCS)_2 \cdot H_2O]$	42.5	3.4	24.2	11.7	43.0	3.6	24.5	11.6	137
$[Mn(pyO)_3(NCSe)_2 \cdot H_2O]$	36.1	3.3	36.6	9.6	35.9	3.0	37.0	9.7	145
$[Co(pyO)_3(NCS)_2 \cdot H_2O]$	42.9	3.6	23.9	12.2	42.7	3.6	24.3	12.3	128
$[Co(pyO)_3(NCSe)_2 \cdot H_2O]$	36.3	3.0	36.5	10.3	35.7	3.0	36.7	10.3	136
$[Ni(pyO)_3(NCS)_2 \cdot H_2O]$	42.9	3.7		12.0	42.7	3.6		12.3	157
$[Ni(pyO)_3(NCSe)_2 \cdot H_2O]$	35.9	3.4		10.3	35.7	3.0		10.3	127
$[Co(pyO)_2(NCS)_2 \cdot EtOH]$	40.7	4.0	27.8	14.3	40.9	3.9	28.3	14.3	90
$[Ni(pyO)_2(NCS)_2 \cdot EtOH]$	40.9	4.0	28.1	14.3	40.9	3.9	28.3	14.3	120
$[Co(pyO)_2(NCS)_2]$	40.6	2.5	31.6	16.2	39.5	2.7	31.8	16.1	161
$[Co(pyO)_2(NCSe)_2]$	31.8	2.1	45.4	12.6	31.4	2.2	45.7	12.8	150
$[Co(pyO)(NCS)_2]$	31.9	2.0	42.6	21.9	31.1	1.9	43.0	21.8	224
$[Cu(pyO)_2(NCS)_2]^a$	38.8	2.7	31.0		38.2	2.7	31.4		179
$[Zn(pyO)_3(NCS)_2]$	43.5	3.3	25.1	13.9	43.7	3.2	24.9	14.0	140
$[Zn(pyO)_3(NCSe)_2]$	36.4	2.9	37.1	11.5	36.4	2.7	37.4	11.7	129
$[Co(qno)_3(NCS)_2]$	56.4	3.7	19.0	9.6	57.1	3.5	19.0	9.7	170
$[Co(qno)_3(NCSe)_2]$	48.9	3.2	30.0	8.5	49.5	3.0	29.8	8.4	136
$[Mn(qno)_3(NCSe)_2]$	47.6	2.7	30.0	7.6	49.8	3.0	30.0	7.9	175
$[Mn(qno)_2(NCS)_2]$ (I)	52.3	3.5	24.9	11.7	52.1	3.1	25.2	11.9	222
$[Mn(qno)_2(NCS)_2]$ (II)	50.5	3.3	24.8	11.7	52.1	3.1	25.2	11.9	131
$[Ni(qno)_2(NCS)_2]$	51.0	3.3	24.8	12.5	51.6	3.0	25.0	12.6	228
$[Ni(qno)_2(NCSe)_2]$	42.1	2.2	37.2	10.1	43.0	2.5	37.6	10.5	134

pyo = Pyridine *N*-oxide and qno = quinoline *N*-oxide.

^a Ref. 8.

RESULTS

Analytical and spectroscopic data for the complexes are given in Tables 1—3. Nitrogen-oxygen stretching frequencies for quinoline *N*-oxide complexes are not included in Table 2 as the N-O stretching vibration is strongly

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³ D. H. Brown, D. Kenyon, and D. W. A. Sharp, *J. Chem. Soc. (A)*, 1969, 1474.

metal ions. In the two ethanol complexes the octahedral structure must be achieved through bridging ethanol or pyridine *N*-oxide ligands. Removal of the ethanol yields a product containing bridging thiocyanato-ligands (see

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⁶ H. Shindo, *Chem. and Pharm. Bull. (Japan)*, 1960, **8**, 845.

⁷ J. H. Nelson, L. C. Nathan, and R. O. Ragsdale, *Inorg. Chem.*, 1968, **7**, 1840.

TABLE 2

I.r. spectra, 4 000—200 cm^{-1} (Nujol mulls)

Complex	$\nu(\text{C-N})$	$\nu(\text{N-O})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$	Other bands
[Co(py ₄)(NCS) ₂]	2 088s 2 079s	1 221s 1 210sh	321m 301m	265s	$\nu(\text{C-S})$ 792w?
[Mn(py ₃ (NCS) ₂ H ₂ O)]	2 078s	1 216s 1 199sh	330s, br	230s	
[Mn(py ₃ (NCSe) ₂ H ₂ O)]	2 075s	1 218s 1 200sh	330s, br		$\delta(\text{NCSe})$ 420w
[Co(py ₃ (NCS) ₂ H ₂ O)]	2 089s	1 215s 1 201s	350s 310m, sh	230m	$\nu(\text{C-S})$ 795w?
[Co(py ₃ (NCSe) ₂ H ₂ O)]	2 085s	1 215s 1 200s	350s 308m, sh		$\delta(\text{NCSe})$ 425w
[Ni(py ₃ (NCS) ₂ H ₂ O)]	2 098s	1 220sh 1 208s	370sh 355s 320sh	255s, br	$\nu(\text{C-S})$ 800w?
[Ni(py ₃ (NCSe) ₂ H ₂ O)]	2 099s	1 215sh 1 205s	375sh 355s 318m	230m	$\delta(\text{NCSe})$ 428w
[Co(py ₂ (NCS) ₂ EtOH)]	2 075s	1 208s	382m	269s	$\nu(\text{C-S})$ 805w?
[Ni(py ₂ (NCS) ₂ EtOH)]	2 095sh 2 082s	1 211s	395m	280s	$\nu(\text{C-S})$ 808w
[Co(py ₂ (NCS) ₂)]	2 119s	1 210sh 1 201s	358m	265s	
[Co(py ₂ (NCSe) ₂)]	2 119s	1 211s 1 200s	360m	235m	$\delta(\text{NCSe})$ 427w
[Co(py)(NCS) ₂]	2 120s	1 212sh 1 200s	356m	270ms	
[Cu(py ₂ (NCS) ₂)]	2 112s	1 200s	390s	331s 248s	$\delta(\text{NCS})$ 455w, 445w
[Zn(py ₃ (NCS) ₂)]	2 075s	1 238s 1 230sh	305sh	280s, br	
[Zn(py ₃ (NCSe) ₂)]	2 070s	1 237s 1 230sh	305m, br	235s, br	$\delta(\text{NCSe})$ 428w
[Co(qno) ₃ (NCS) ₂]	2 061s 2 050sh		360s	299s	310sh, 280sh, ligand
[Co(qno) ₂ (NCSe) ₂]	2 080s 2 060m		360m	255m, br	310, ligand
[Mn(qno) ₃ (NCSe) ₂]	2 062s		345s	245m	310, 280, ligand
[Mn(qno) ₂ (NCS) ₂] (I)	2 100s 2 055s		365m 330s	260s	310, ligand
(II)	2 045s		328s		310sh, ligand 265w?
[Ni(qno) ₂ (NCS) ₂]	2 070s		340s	235s	
[Ni(qno) ₂ (NCSe) ₂]	2 068s		340s		

s = Strong, w = weak, br = broad, and sh = shoulder.

TABLE 3

Visible spectra (Nujol mulls)

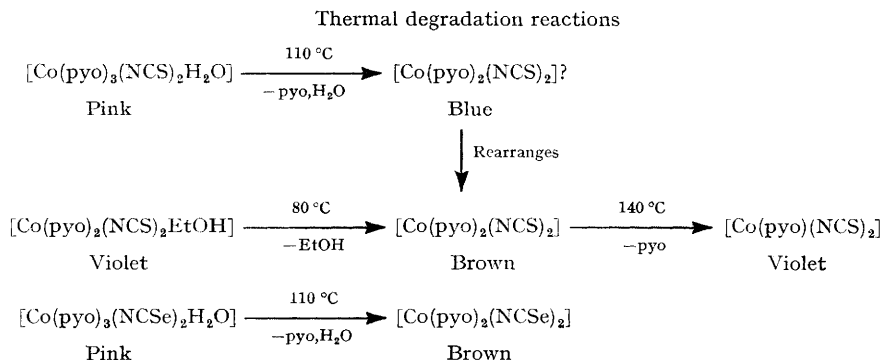
Complex	Wavenumbers of absorption maxima/ cm^{-1}	Colour
[Co(py ₄)(NCS) ₂]	7 200, 15 500, 19 200	Pink
[Mn(py ₃ (NCS) ₂ H ₂ O)]	21 400	Yellow
[Mn(py ₃ (NCSe) ₂ H ₂ O)]	21 000	Yellow
[Co(py ₃ (NCS) ₂ H ₂ O)]	8 200, 14 800, 19 500	Pink
[Co(py ₃ (NCSe) ₂ H ₂ O)]	8 300, 15 400, 19 800	Pink
[Ni(py ₃ (NCS) ₂ H ₂ O)]	8 200, 14 800 ^b	Green
[Ni(py ₃ (NCSe) ₂ H ₂ O)]	8 400, 15 000 ^b	Green
[Co(py ₂ (NCS) ₂ EtOH)]	7 800, 15 900, 18 200; 19 800sh	Violet
[Ni(py ₂ (NCS) ₂ EtOH)]	8 300, 13 200sh, 14 400 ^b	Green
[Co(py ₂ (NCS) ₂)]	8 800, 16 700, 18 200, 19 200, 21 200	Brown
[Co(py ₂ (NCSe) ₂)]	8 700, 16 300, 18 400, 19 300, 21 200	Brown
[Co(py)(NCS) ₂]	6 600, 7 400sh, 16 400sh, 17 600, 18 400, 19 300sh	Violet
[Cu(py ₂ (NCS) ₂)]	13 200	Green
[Co(qno) ₃ (NCS) ₂]	7 600, 15 800sh(vs), 20 600	Deep blue
[Co(qno) ₃ (NCSe) ₂]	8 200, 16 000sh(vs), 17 000sh	Deep blue
[Mn(qno) ₃ (NCSe) ₂]	18 600, 20 200sh, 22 400 ^c	Orange
[Mn(qno) ₂ (NCS) ₂] (I)	18 800sh, 20 200sh, 21 500, 22 600 ^c	Orange
(II)	18 800 sh, 20 200, 21 500, 22 400 ^c	Orange
[Ni(qno) ₂ (NCS) ₂]	8 300, 14 400 ^b	Pale brown
[Ni(qno) ₂ (NCSe) ₂]	8 400, 14 600 ^b	Pale brown

Ref. 20. ^b $^3T_{1g}(P) \leftarrow ^3A_{2g}$ Obscured by c.t. band. ^c These bands may be associated with the c.t. absorption (ref. 21).

below), suggesting that ethanol is directly co-ordinated to the metal in the parent complex and possibly functions as the bridging group.

$[\text{Co}(\text{pyo})_2(\text{NCX})_2]$ and $[\text{Co}(\text{pyo})(\text{NCS})_2]$.—These complexes were prepared by thermal degradation of the aquo- and ethanol complexes. The bis(pyridine *N*-oxide) complexes were also obtained by precipitation methods. The complex $[\text{Co}(\text{pyo})_3(\text{NCS})_2\text{H}_2\text{O}]$ loses water and one pyo molecule at 110 °C to form initially an unstable

tions at *ca.* 16 000 cm^{-1} ($\epsilon \simeq 1\,500\text{--}2\,000\text{ l mol}^{-1}\text{ cm}^{-1}$ in nitromethane, slow decomp.) assigned to ${}^4T_1(P) \leftarrow {}^4A_2$ transitions in the tetrahedral $[\text{Co}(\text{NCX})_4]^{2-}$ ions.^{18,19} The manganese and cobalt selenocyanato-complexes are isomorphous. The manganese complex is bright orange because of the overlap of a c.t. band into the visible part of the spectrum.^{20,21} The i.r. spectra are consistent with those reported elsewhere for complexes containing the $[\text{M}(\text{qno})_6]^{2+}$ or $[\text{M}(\text{NCX})_4]^{2-}$ ($\text{M} = \text{Co}$ or Mn) ions.^{7,15,17,21}



bright blue product which rapidly transforms to the stable brown complex $[\text{Co}(\text{pyo})_2(\text{NCS})_2]$. Visible and i.r. spectra of this complex indicate an octahedral structure with bridging thiocyanato-ligands. We were unable to isolate the intermediate complex, but its intense colour and mode of formation suggest that it is a monomeric tetrahedral isomer of $[\text{Co}(\text{pyo})_2(\text{NCS})_2]$. The aquo-selenocyanato-complex degrades directly to selenocyanato-bridged $[\text{Co}(\text{pyo})_2(\text{NCSe})_2]$ with no sign of a similar tetrahedral intermediate. The thiocyanato-complex loses a second pyo molecule at 140 °C to form $[\text{Co}(\text{pyo})(\text{NCS})_2]$, in which we would expect all three ligand groups to occupy bridging positions. The analogous nickel(II) complexes appeared to undergo similar thermal degradation reactions, but gave generally less-satisfactory analytical data for the reaction products.

$[\text{Cu}(\text{pyo})_2(\text{NCS})_2]$ and $[\text{Zn}(\text{pyo})_3(\text{NCX})_2]$.—The copper complex may be assigned a six-co-ordinate thiocyanato-bridged structure on the evidence of its normal magnetic moment;^{8,9} the C–N stretching frequency ($2\,112\text{ cm}^{-1}$) is consistent with this structure. Zinc halides usually react with pyo to form tetrahedral species $[\text{Zn}(\text{pyo})_2\text{X}_2]$,^{10,11} but the stoichiometry of the pseudohalide complexes suggests an ionic formulation $[\text{Zn}(\text{pyo})_6][\text{Zn}(\text{NCX})_4]$. The C–N, N–O, Zn–O, and Zn–N stretching frequencies are similar to those reported for the $[\text{Zn}(\text{pyo})_6]^{2+}$ and $[\text{Zn}(\text{NCX})_4]^{2-}$ ions.^{12–17}

$[\text{Co}(\text{qno})_3(\text{NCX})_2]$ and $[\text{Mn}(\text{qno})_3(\text{NCSe})_2]$ $\{[\text{M}-\text{qno}]_6-[\text{M}(\text{NCX})_4]\}$.—The cobalt complexes have intense absorp-

$[\text{Mn}(\text{qno})_2(\text{NCS})_2]$.—Two complexes of this composition were isolated, with substantially different m.p.s, *X*-ray powder diffraction patterns, and i.r. spectra. The Mn–N stretching frequency in isomer (I) (260 cm^{-1}) is closer to that in tetrahedral $[\text{Mn}(\text{NCS})_4]^{2-}$ (284 cm^{-1}) than octahedral $[\text{Mn}(\text{NCS})_6]^{4-}$ (222 cm^{-1}).¹⁵ This complex exhibits two very sharp C–N stretching bands ($2\,100\text{--}2\,055\text{ cm}^{-1}$) but it is not possible to determine its structure from the i.r. data alone. The second isomer (II) has a single C–N stretching band ($2\,045\text{ cm}^{-1}$) typical of ionic thiocyanate⁵ and there appears to be no far-i.r. band which can be assigned to a Mn–N stretching vibration. Therefore, we suggest that this isomer has an ionic structure, with the manganese ions most probably tetrahedrally co-ordinated by bridging qno ligands. Both isomers dissolve in nitromethane but appear to dissociate in the process, as the resulting solutions are colourless.

$[\text{Ni}(\text{qno})_2(\text{NCX})_2]$.—These pale brown, paramagnetic complexes $\{[\text{Ni}(\text{qno})_2(\text{NCS})_2] \mu_{\text{eff}} \text{ ca. } 2.93\text{ B.M.}\}$ have visible absorptions at frequencies typical of octahedrally co-ordinated nickel(II). The C–N stretching frequencies are in the usual region for the terminal, *N*-bonded pseudohalides and the qno molecules presumably function as bridging ligands.

DISCUSSION

There are few direct analogies between the series of complexes formed by the two ligands; in particular,

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¹⁷ A. Sabatini and I. Bertini, *Inorg. Chem.*, 1965, **4**, 959.

¹⁸ F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and A. Sacco, *J. Amer. Chem. Soc.*, 1961, **83**, 4157.

¹⁹ F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and T. E. Haas, *Inorg. Chem.*, 1962, **1**, 565.

²⁰ R. L. Carlin, *J. Amer. Chem. Soc.*, 1961, **83**, 3773.

²¹ L. C. Nathan and R. O. Ragsdale, *Inorg. Chim. Acta.*, 1969, **3**, 473.

we were unable to prepare quinoline *N*-oxide aquo- or ethanol complexes corresponding to those readily obtained with pyridine *N*-oxide. Quinoline *N*-oxide has a slightly higher pK_a value than pyridine *N*-oxide (qno 0.86, pyo 0.79) and is also rather the better π -bonding ligand,⁷ so that it may compete more effectively with solvent molecules for co-ordination sites, but in most cases we would expect lattice energies and the steric requirements of the ligands to determine which complexes separate as stable solid species. In general, the structures proposed for the pseudohalide complexes are similar to those found, or postulated, for the corresponding halides.¹⁻³ There is no evidence for the formation of terminal S- or Se-bonded pseudohalide species.

The assignments of M-O and M-N vibrations in Table 2 may be questioned on the grounds that these vibrations are likely to interact in molecules or ions containing M-O and M-N bonds. However, the 'M-O' frequencies are generally similar to those observed in $[M(\text{pyo})_6]^{2+}$ and $[M(\text{qno})_6]^{2+}$ species (300–400 cm^{-1})^{12-14, 21, 22} and it seems fair to assume that bands in this region have a predominant M-O stretching contribution. The M-N stretching frequencies are comparable with those in other metal-pseudohalide complexes.^{15-17, 23} The metal-ligand frequencies increase in the usual order $M = \text{Mn} < \text{Co} < \text{Ni} < \text{Cu} > \text{Zn}$ in comparable complexes.

The pseudohalide-bridged octahedral complexes $[\text{Co}(\text{pyo})_2(\text{NCS})_2]$ and $[\text{Cu}(\text{pyo})_2(\text{NCS})_2]$ are interesting because the stoichiometrically analogous pyridine (py) complexes have been studied in some detail.²⁴ Clark and Williams²³ assign a Co-NCS stretching vibration in $[\text{Co}(\text{py})_2(\text{NCS})_2]$ at 268 cm^{-1} , corresponding to the 265 cm^{-1} band in $[\text{Co}(\text{pyo})_2(\text{NCS})_2]$. The complex $[\text{Cu}(\text{py})_2(\text{NCS})_2]$ has bands at 319 and 214 cm^{-1} assigned to copper-thiocyanate modes, and a copper-pyridine stretch at 256 cm^{-1} . In the *N*-oxide complex we observe $\nu(\text{Cu-O})$ at 390 cm^{-1} and two further bands at 331 and 248 cm^{-1} which we assign to copper-thiocyanate vibrations [approximately, $\nu(\text{Cu-NCS})$ and $\nu(\text{Cu-SCN})$]. There is no evidence (above 200 cm^{-1}) of any absorption corresponding to the 214 cm^{-1} band in the complex $[\text{Cu}(\text{py})_2(\text{NCS})_2]$. Clark and Williams' assignments for $[\text{Cu}(\text{py})_2(\text{NCS})_2]$ are consistent with those for other copper-amine complexes; the apparent discrepancies between the spectra of the py and pyo

complexes are most probably due to rather large differences in the copper environment in the two complexes.

The complex *trans*- $[\text{Co}(\text{py})_4(\text{NCS})_2]$ ²⁵ has a Co-NCS stretching band²³ at 270 cm^{-1} and cobalt-pyridine bands at 215 and 205 cm^{-1} . The spectrum of $[\text{Co}(\text{pyo})_4(\text{NCS})_2]$ is qualitatively similar, with $\nu(\text{Co-O})$ at 321 and 301 cm^{-1} and $\nu(\text{Co-NCS})$ at 265 cm^{-1} . Some splitting of the Co-O mode is to be expected as the Co-O-N arrangement is necessarily non-linear and the molecular symmetry will be lower than D_{4h} even in a *trans*-complex.²⁶ A *cis*-complex should give rise to a much more complicated metal-ligand spectrum and we conclude that the *N*-oxide complex also has the *trans*-structure.

EXPERIMENTAL

Preparation of Complexes.—From solution. The complexes listed below precipitated or crystallised slowly on mixing metal pseudohalide and ligand in appropriate ratios in a suitable solvent. The products were washed with the same solvent and dried *in vacuo*. Details of solvents, acceptor:donor ratios, and any special precautions are summarised below. $[\text{M}(\text{pyo})_3(\text{NCS})_2 \cdot \text{H}_2\text{O}]$ ($M = \text{Co}$ or Ni) and $[\text{Ni}(\text{qno})_2(\text{NCSe})_2]$: acetone 1:6. $[\text{Mn}(\text{pyo})_3(\text{NCX})_2 \cdot \text{H}_2\text{O}]$, $[\text{Zn}(\text{pyo})_3(\text{NCX})_2]$, $[\text{M}(\text{qno})_3(\text{NCSe})_2]$ ($M = \text{Co}$ or Mn), and $[\text{Ni}(\text{qno})_2(\text{NCS})_2]$: ethanol, 1:6. $[\text{Co}(\text{qno})_3(\text{NCS})_2]$: *n*-butyl alcohol, 1:6. $[\text{M}(\text{pyo})_2(\text{NCS})_2 \cdot \text{EtOH}]$ ($M = \text{Co}$ or Ni) and $[\text{Co}(\text{pyo})_2(\text{NCSe})_2]$: ethanol, 1:1. $[\text{Cu}(\text{pyo})_2(\text{NCS})_2]$: ethanol, 1:1–1:10. $[\text{Co}(\text{pyo})_2(\text{NCS})_2]$: from hot concentrated ethanol, 1:1. $[\text{Co}(\text{pyo})_4(\text{NCS})_2]$: anhydrous ethanol and reagents, dry-box, 1:4. $[\text{Mn}(\text{qno})_2(\text{NCS})_2]$: form (I) from ethanol, 1:6, by slow crystallisation (3 days); form (II) from ethanol, 1:6, after rapid removal of ethanol on a rotary evaporator.

Thermal degradation experiments. These were carried out in an evacuated pistol. Volatile products were collected in a cold-trap and identified by their i.r. spectra. Weight losses of the samples were quantitative in terms of the reaction schemes in the text.

X-Ray powder diffraction measurements were made using a Phillips PW 1051 recording powder diffractometer with $\text{Cu-K}\alpha$ radiation. The following isomorphous series were identified: $[\text{M}(\text{pyo})_3(\text{NCS})_2 \cdot \text{H}_2\text{O}]$ ($M = \text{Mn}$, Co , or Ni); $[\text{M}(\text{pyo})_3(\text{NCSe})_2 \cdot \text{H}_2\text{O}]$ ($M = \text{Mn}$, Co , or Ni); $[\text{Co}(\text{pyo})_2(\text{NCX})_2]$ ($X = \text{S}$ or Se), $[\text{Zn}(\text{pyo})_3(\text{NCX})_2]$ ($X = \text{S}$ or Se); and $[\text{M}(\text{qno})_3(\text{NCSe})_2]$ ($M = \text{Mn}$ or Co). I.r. and visible spectra were obtained using mineral-oil mulls with Perkin-Elmer 457 and 225, and Unicam SP 700 spectrophotometers, respectively.

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