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SYNTHESIS AND THERMAL BEHAVIOUR OF MORPHOLINE COMPLEXES WITH COBALT (II) AND MANGANESE (II) THIOCYANATES

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The 1 : 4 complexes of cobalt (II) and manganese (II) thiocyanates with morpholine (Morph), $[M(NCS)_2(Morph)_4]$ (M = Co, Mn), were prepared and studied by means of thermogravimetry, derivative thermogravimetry and differential scanning calorimetry. By thermal treatment of the above compounds, the 1 : 2 and 1 : 1 complexes, $[M(NCS)_2(Morph)_2]$ (M=Co, Mn; n=1, 2), were formed. Magnetic data, infrared and electronic spectra and molar conductance values for the compounds are reported. All the complexes contain N-bonded morpholine and the 1 : 4 complexes are suggested to have a monomeric *cis* pseudooctahedral structure with N-bonded thiocyanate, whereas the 1 : 2 and 1 : 1 complexes are considered to have a six-coordinated polymeric configuration involving bridging NCS groups.

Morpholine is used extensively as a corrosion inhibitor in steam boiler systems. In this respect it is of interest to study the interactions between morpholine and transition metals usually present in technical alloys [1].

Several studies have been made on the preparation and structural characterization of coordination compounds formed by interaction of morpholine with cobalt(II) [2, 3] and manganese(II) [2] halides, but for the $M(NCS)_2$-morpholine system (M = Co, Mn) only the synthesis of $[Co(NCS)_2(Morph)_2]$ has been described [3].

We report here on the preparation and thermal study of $[M(NCS)_2(Morph)_4]$ (M = Co, Mn). As in the case of the nickel analogue [4], thermogravimetry has been used as a method for the detection and isolation of polymeric structures which cannot be prepared by other methods. Thus, $[M(NCS)_2(Morph)_2]$ and $[M(NCS)_2(Morph)]$, obtained by thermal treatment of $[M(NCS)_2(Morph)_4]$ (M = Co, Mn), contain NCS bridges, and morpholine appears to act as a bidentate (N- and O-donor) ligand in $[M(NCS)_2(Morph)]$.

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Experimental

Materials and methods

Morpholine and 2,2-dimethoxypropane were obtained from May and Baker Ltd. and Fluka, respectively, and used as such. Methanol solutions ($c \simeq 0.23$ *M*) of cobalt(II) thiocyanate were prepared through the metathetic reaction between $Co(NO_3)_2 \cdot 6H_2O$ and KSCN in methanol and removal of the precipitated potassium nitrate by filtration. Anhydrous manganese thiocyanate was prepared as described elsewhere [5]. The solvents were dried before use, by methods described in the literature.

The C, H and N analyses were performed with a Perkin–Elmer 240C microanalyzer. Cobalt and manganese were determined by titration with EDTA [6]. IR spectra were recorded in the range 4000–200 cm^{-1} on a Perkin–Elmer 1430 spectrophotometer, with samples as Nujol mulls between polyethylene sheets. Electronic spectra were recorded on a Beckman DK–2A instrument (solids) or a Hitachi U2300 instrument (acetone solutions). Magnetic susceptibilities were measured by the Faraday method, using a Cahn RG 2102 electrobalance and a Systron Conner 6001 electromagnet calibrated with $Hg[Co(NCS)_4]$ [7]. Thermal decomposition studies were carried out on a Mettler TG–50 thermobalance and a Mettler DSC–20 calorimeter. Conductivities were measured with a Philips PW 9501/01 conductimeter.

Preparation of the complexes

$[Co(NCS)_2(Morph)_4]$. Morpholine (4 cm^3; 46 mmol) was added to a methanolic solution of cobalt(II) thiocyanate (10 cm^3 of 0.23 *M* solution). After stirring for 24 h, the resulting pink-violet precipitate was suction-filtered, washed with diethyl ether and dried in air. Yield = 55%.

$[Mn(NCS)_2(Morph)_4]$. A mixture of morpholine (1.5 cm^3; 17.2 mmol) and 2,2-dimethoxypropane (1.5 cm^3) was added to manganese thiocyanate (0.4 g; 2.34 mmol) and the resulting suspension was vigorously stirred under a N_2 atmosphere, washed with diethyl ether and dried under vacuum. Yield = 50%. A progressive darkening of the product was observed on prolonged exposure to air.

$[M(NCS)_2(Morph)_n]$ (M = Co, Mn; $n = 1, 2$). These compounds were obtained by heating the corresponding compounds $[M(NCS)_2(Morph)_4]$ as described below.

Results

The corresponding metal thiocyanates react with morpholine to give the 1 : 4 complexes $[M(NCS)_2(Morph)_4]$ (M = Co, Mn), but, in the case of manganese, oxygen and moisture must be excluded from the reaction medium. Their colours and analytical data are listed in Table 1. The manganese compound decomposes progressively on exposure to air; moreover, there is infrared evidence (see below) that, on prolonged storage under a static N_2 atmosphere, some morpholine is released from the coordination sphere of manganese(II).

Table 1 Colours, analytical data and molar conductances for the cobalt and manganese compounds

Compound		Analysis, % (found (calc.)				$\Lambda_M{}^a$, ohm^{-1} cm^2 mol^{-1}
		Metal	C	H	N	
$[Co(NCS)_2(Morph)_4]$	pink-violet	11.3	41.0	6.8	16.0	57
		(11.3)	(41.3)	(6.9)	(16.1)	
$[Co(NCS)_2(Morph)_2]$	pink		34.5	5.3	16.2	60
			(34.7)	(5.4)	(16.2)	
$[Co(NCS)_2(Morph)]$	bluish-grey		27.4	3.5	16.0	68
			(27.5)	(3.4)	(16.0)	
$[Mn(NCS)_2(Morph)_4]$	pale-pink	10.5	41.4	6.8	16.0	68.5
		(10.6)	(41.6)	(6.9)	(16.2)	
$[Mn(NCS)_2(Morph)_2]$	pale-pink		34.8	5.3	16.0	75
			(34.8)	(5.2)	(16.2)	
$[Mn(NCS)_2(Morph)]$	white		27.7	3.6	16.2	55
			(27.9)	(3.5)	(16.3)	

[a] In acetone solution, $c = 5 \times 10^{-4}$ *M*.

The thermogravimetric (TG) and differential scanning calorimetry (DSC) traces for $[M(NCS)_2(Morph)_4]$ (M = Co, Mn) are shown in Figs 1 and 2, respectively. $[Co(NCS)_2(Morph)_4]$ decomposes between 342 and 408 K (DTG peak at 393 K) to give $[Co(NCS)_2(Morph)_2]$, which is stable up to 413 K. The latter compound decomposes between 413 and 476 K (DTG peak at 456 K) and $[Co(NCS)_2(Morph)]$ is formed in this stage; this compound is stable up to 493 K. The experimental weight losses (32.8 and 16.3%, respectively) are in agreement with the theoretical ones (33.3 and 16.6%, respectively) for the proposed processes.

$[Mn)NCS)_2(Morph)_4]$ is stable up to 338 K, although it loses weight slowly from room temperature. In the range 338–387 K (DTG peak at 379 K), $[Mn(NCS)_2(Morph)_2]$ is formed, which decomposes between 393 and 426 K (DTG peak at 418 K) to give $[Mn(NCS)_2(Morph)]$. The overall weight loss is 50.2% (theoretical value for three morpholine molecules, 50.3%). The weight loss in the

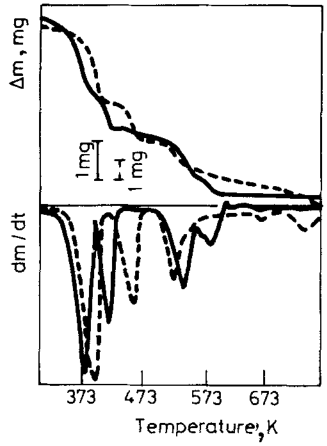

Fig. 1 TG and DTG traces for the thermal decomposition (in N_2) of: (a) $[Co(NCS)_2(Morph)_4]$ (- - -), 13.39 mg; (b) $[Mn(NCS)_2(Morph)_4]$ (——), 8.76 mg

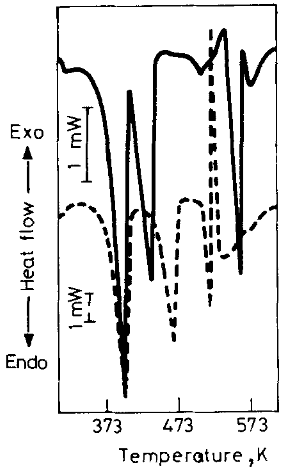

Fig. 2 DSC traces for $[Co(NCS)_2(Morph)_4]$ (- - -) and $[Mn(NCS)_2(Morph)_4]$ (——)

first decomposition stage is slightly smaller under dynamic heating than the theoretical one corresponding to two morpholine molecules (32,2% *vs.* 33.5%, respectively), but under constant heating (363 K) a closer value is obtained (33,2%). Except for the 1 : 1 complexes, where the manganese compound decomposes at a slightly higher temperature, the 1 : 4 and 1 : 2 cobalt compounds are more stable than the manganese ones, which is in agreement with the general trends in the relative stabilities of comparable compounds of these elements.

For both compounds $[M(NCS)_2(Morph)_4]$ (M = Co, Mn), the three thermal decomposition stages are endothermic, with DSC peaks at 399, 467 and 520 K (cobalt compound), and 394, 432 and 558 K (manganese compound). The cobalt compound shows an additional exothermic peak at 523 K. For each compound, the estimated reaction enthalpies corresponding to the first two stages are 60.5 and 88.2 kJ per mol of morpholine (Co), and 55.0 and 73.0 kJ per mol of morpholine (Mn).

Table 2 Magnetic moments and electronic spectra of the cobalt compounds

Compound	μ_{eff}, BM	Electronic bands, $cm^{-1} \times 10^{-3}$[a]
$[Co(NCS)_2(Morph)_4]$	5.17	Solid: 8.0sh, 8.9; 17.8, 18.8, 19.7 Me_2CO soln: 16.2 (930), 17.7sh
$[Co(NCS)_2(Morph)_2]$	5.05	Solid: 7.9sh, 9.2; 17.5, 18.5 Me_2CO soln.: 16.1 (1005), 17.5sh
$[Co(NCS)_2(Morph)]$	4.95	Solid: 7.7, 9.0; 16.4sh, 17.4, 18.6 Me_2CO soln.: 16.1 (895), 17.6sh

[a] Values in parentheses are molar extinction coefficients (cm^{-1} mol^{-1} L).

The room-temperature magnetic moments (Table 2) of the cobalt compounds lie in the range 4.7–5.2 BM, which covers the value expected for all spin-free, octahedral cobalt(II) complexes possessing an orbitally degenerate $^4T_{1g}$ ground term with an orbital contribution to the magnetic moment [8]. The reflectance spectra (Table 2) show two split bands, which can be interpreted [9] in terms of a distorted octahedral coordination sphere: they are assigned to the $\nu_1[^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)]$ and $\nu_3[^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)]$ transitions in O_h symmetry. However, in acetone solution the compounds give the characteristic absorption of tetrahedrally coordinated cobalt(II), $^4A_2(F) \rightarrow {}^4T_1(P)$, and the molar conductance values of the deep-blue solutions (Table 1) are approximately half of the value for 1 : 1 electrolytes [10], indicating that partial dissociation of the complexes may have occurred via certain of the mechanisms proposed for similar thiocyanates complexes [11].

The electronic spectra of the manganese compounds were not well resolved and no interpretation could be attempted. In acetone solution, the molar conductances of the manganese compounds are similar to those observed for the cobalt compounds (Table 1).

Some infrared absorptions which are important for structural study are listed in Table 3. In all cases, the drop of 70–80 cm^{-1} observed for the N–H stretching shows that morpholine is coordinated to the metal ion through the nitrogen atom. As in previous papers [12, 13], the C–N and C–O stretching modes of morpholine are found at ca. 1095 and 1030 cm^{-1}, respectively [14]. The infrared spectra of

Table 3 Relevant infrared data (cm^{-1}) for the cobalt and manganese compounds

Compound	NH str.	NCS			
		NC str.	CS str.	NCS def.	M–NCS str.
$[Co(NCS)_2(Morph)_4]$	3230sh	2100vs, br	805m	470m	275sh
	3210s		785m		270m, br
$[Co(NCS)_2(Morph)_2]$	3230s	2100vs	785m	475m	265m
		2060sh		465m	
$[Co(NCS)_2(Morph)]$	3220w	2100vs	790m	480m	270m
		2060sh		470m	
$[Mn(NCS)_2(Morph)_4]$	3230m	2090vs	795w	470m	255m
	3200m	2080vs	780m	465m	250m
$[Mn(NCS)_2(Morph)_2]$	3220s	2095vs	780m	475m	255m
				465sh	
$[Mn(NCS)_2(Morph)]$	3230w	2090vs	785w	470m	260m
				460m	
Free morpholine	3298				
[14]	(3336)[a]				

[a] Value for the equatorial conformer

$[M(NCS)_2(Morph)_n]$ (M = Co, Mn; $n = 1, 2$) exhibit absorption bands in the regions 2100, 790–780 and 480–460 cm^{-1}, which are identified as $\nu(CN)$, $\nu(CS)$ and $\delta(NCS)$ modes, respectively, due to coordinated thiocyanate groups; their wavenumbers are in good agreement with those of similar modes in transition-metal complexes which have only bridging thiocyanate groups [15–17]. However, the compounds $[M(NCS)_2(Morph)_4]$ (M = Co, Mn) give an additional band at ca. 800 cm^{-1} for $\nu(CS)$, which is consistent with the presence of terminal N-bonded thiocyanate [18] (two bands are also observed for the N–H stretching mode in these compounds). All the compounds give an absorption at 270–250 cm^{-1}, attributed to the $\nu(M\text{–}NCS)$ vibration [19], which in the 1 : 4 complexes is observed either as a double band (Mn) or as a rather broad band with a shoulder (Co).

On the basis of the above data, a six-coordinate, polymeric tetragonal configuration involving bridging NCS is assigned to $[M(NCS)_2(Morph)_2]$ (M = Co, Mn), while a similar structure, possibly with both bridging NCS and bridging morpholine, may be attributed to $[M(NCS)_2(Morph)]$ (M = Co, Mn). A pseudooctahedral structure containing the NCS groups in *cis* positions is proposed for the compounds $[M(NCS)_2(Morph)_4]$ (M = Co, Mn).

When $[Mn(NCS)_2(Morph)_4]$ was kept in a desiccator under a static N_2 atmosphere, after ca. 1 week the infrared spectrum showed four bands with the same intensity at 2100, 2080, 2050 and 2020 cm^{-1} for $\nu(NC)$ of the thiocyanate group, two bands at 3290 (N–H stretch of free morpholine) and 3230 (N–H stretch of coordinated morpholine) cm^{-1}, and a complex band with four peaks centred at 250 cm^{-1} for ν(Mn–NCS); the elemental analysis of the pale-pink product showed that the Mn(NCS)$_2$: morpholine molar ratio was 1 : 4. Since the infrared pattern in the region 2100–2020 cm^{-1} is the expected one for a Mn(μ-NCS)$_2$Mn(NCS)$_2$ moiety, which has been found in a great number of bimetallic thiocyanates of the type M(μ-NCS)$_2$M'(NCS)$_2$ [19], the structure [(Morph)$_4$Mn(μ-NCS)$_2$Mn(NCS)$_2$(Morph)$_2$]·2Morph (C$_{2v}$ symmetry; four infrared-active thiocyanate modes) is suggested; this structure in fact represents the first intermediate step towards the polymeric tetragonal structure [Mn(NCS)$_2$(Morph)$_2$]. As mentioned above, under the dynamic N$_2$ atmosphere in the TG experiment [Mn(NCS)$_2$(Morph)$_4$] slowly and progressively loses weight at room temperature and is transformed directly to [Mn(NCS)$_2$(Morph)$_2$] in the temperature range 338–387 K.

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Zusammenfassung — Mittels Thermogravimetrie, Derivativthermogravimetrie und Differential-Scanning-Kalorimetrie wurden die zuvor dargestellten 1:4 Komplexe von Kobalt(II)- und Mangan(II)thiozyanaten mit Morpholin (morph) [$M(NCS)_2(morph)_4$] mit M = Co, Mn untersucht. Durch Erhitzen obiger Verbindungen entstehen die 1:2- bzw. 1:1-Komplexe [$M(NCS)_2(morph)_n$] mit M = Co, Mn und $n = 1, 2$. Magnetisierungsdaten, Infrarot- und Elektronenspektren sowie die molare Leitfähigkeit der Verbindungen wurden ermittelt bzw. angegeben. Alle Komplexe enthalten N-gebundenes Morpholin. Die 1:4 Komplexe besitzen eine monomere cis-pseudooktaedrische Struktur mit N-gebundenem Thiozyanat, während die 1:2- und 1:1-Komplexe eine hexakoordinierte polymere Struktur mit NCS-Gruppenbrücken zu besitzen scheinen.

Резюме — Методом ТГ, ДТГ и ДСК изучены синтезированные комплексы тиоцианатов кобальта и марганца с морфолином (морф.) общей формулы [$M(NCS)_2$(морф.)$_4$]. При термической обработке этих комплексов образуются соединения состава [$M(NCS)_2$(морф.)$_n$], где $n = 1$ или 2. Для этих соединений приведены магнитные данные, ИК спектроскопические данные, электронные спектры поглощения и значения молярной проводимости. Координационная связь в комплексах осуществляется через азот морфолина. Комплексы состава 1:4 (металл : лиганд) являются мономерными с цис-псевдооктаэдрической структурой и содержащие N-связанные тиоцианатные группы. Комплексы состава 1:2 и 1:1 имеют шести-координационную полимерную конфигурацию, включающую мостиковые тиоцианатные группы.