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VARIATION OF PRODUCT IDENTITY AS A FUNCTION OF METAL ION: LIGAND REACTION RATIO, STEREOCHEMICAL STUDIES AND THERMAL INVESTIGATION OF Mn(II), Fe(III), Ni(II), Cu(II), Cd(II) AND Hg(II) COMPLEXES OF 2-ACETYLPYRIDINE HYDRAZONE

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ABSTRACT

A systematic investigation of the MX_2 and $FeCl_3$/APH reaction systems in EtOH is described, where M = Mn, Ni, Cu, Cd and Hg, X = Cl, Br, NO_3, SCN, CH_3COO, BF_4 and $\frac{1}{2}SO_4$, and APH = 2-acetylpyridine hydrazone. Emphasis has been placed on determining the influence of the metal ion : APH ratio on the identity of the reaction products. The variation of this ratio has led to the synthesis of thirty-two new discrete complexes with general compositions $M(APH)X_2$, $M(APH)_2X_2$, $M(APH)_3X_2$, $Fe(APH)Cl_3$ and $Fe(APH)_2Cl_3$. The complexes were characterized by elemental analyses, conductivity measurements, X-ray powder patterns, thermal methods, magnetic susceptibilities and spectroscopic (IR, ligand field, ^1H NMR, ESR) studies. Monomeric pseudo-tetrahedral and monomeric or polymeric distorted octahedral stereochemistries were assigned in the solid state. APH appears to coordinate via both the pyridine and methine nitrogen atoms. The thermal decomposition of the prepared complexes was also studied. Some Ni(II) complexes decompose via stable intermediates. Probable mechanistic paths of the decomposition reactions have been proposed.

INTRODUCTION

It is becoming increasingly apparent that the inorganic chemistry of hydrazones is of great relevance and/or importance to a wide variety of

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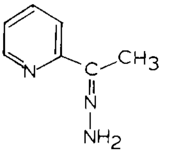
chemical [1,2], biological [3] and industrial [4] systems. The combined developments described in these references show the need for research in the field of the coordination chemistry of hydrazones; this belief represents the primary stimulus for the work described herein. In addition, during routine TG experiments it was found that if some Ni(II) complexes of the title ligand are heated under non-isothermal conditions, they decompose via stable intermediates. The isolation and characterization of these intermediates encouraged us to investigate the mechanistic path of decomposition, as the problems related to the phenomenon of structural change during thermal decomposition of coordination compounds have not been completely explored [5].

Despite the interest in many ligands containing the –N=C–C=N– grouping, the coordination chemistry of hydrazones of 2-pyridyl ketones has received only scant attention [6–10]. This work will concentrate on the preparation, stereochemical studies and thermal decomposition of 2-acetylpyridine hydrazone (APH) complexes with Mn(II), Fe(III), Ni(II), Cu(II), Cd(II) and Hg(II). As we shall describe, we have found that the metal ion : APH reaction ratio has a great effect on the identity of the obtained products. Cobalt(II) and zinc(II) complexes of APH have previously been prepared and studied [10].



APH

EXPERIMENTAL

Elemental analyses, physicochemical measurements and spectroscopic techniques were carried out using published methods [10–12]. APH was synthesized as previously described [10].

Preparation of the metal complexes

The metal salts $FeCl_3$, $MnX_2 \cdot 4H_2O$ (X = Cl, NO_3), $MnBr_2 \cdot H_2O$, NiX_2 $6H_2O$ (X = Cl, NO_3), $NiBr_2 \cdot 3H_2O$, $Ni(NCS)_2$, CuX_2 (X = Cl, Br, BF_4), $Cu(NO_3)_2 \cdot 3H_2O$, $Cu(CH_3COO)_2 \cdot H_2O$, $CuSO_4 \cdot 5H_2O$, $CdX_2 \cdot 4H_2O$ (X = Br, NO_3), CdI_2 and HgX_2 (X = Cl, Br) were used as starting materials.

One general method of preparation of complexes was used. The method involved the direct reaction of an ethanolic (methanolic in the case of $Ni(NCS)_2$) solution of the appropriate metal salt with a solution of the required amount of APH in a small volume of absolute ethanol under reflux for 45 min (for molar ratios, see Table 1). When hydrated metal salts were used as starting materials, a few ml of triethyl orthoformate (TEOF) were added to the reaction mixtures for dehydration purposes. Solid product formation was usually very rapid (2–5 min), although the complexes $Fe(APH)_nCl_3$ ($n = 1,2$) and $Cu(APH)_2X_2$ ($X = Cl, Br$) were deposited slowly during the reflux and crystallization was completed by cooling the mixtures in the refrigerator overnight. The precipitates were collected by filtration and washed with absolute ethanol and ether. They were stirred again in warm absolute ethanol to remove unreacted starting materials, then filtered off, washed as above and dried in a vacuum over silica gel.

RESULTS AND DISCUSSION

Synthesis

Our programme of syntheses in terms of changing the metal ion : APH molar ratio are described in Table 1. In general, for a given metal salt both 1 : 1 and 1 : 2 complexes can be isolated. Exceptions are $Mn(NO_3)_2 \cdot 4H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ which yield only 1 : 2 complexes, $CuSO_4 \cdot 5H_2O$ which yields no 1 : 1 complex and $Cu(CH_3COO)_2 \cdot H_2O$, $CdBr_2 \cdot 4H_2O$ and Hg(II) salts which yield only 1 : 1 complexes irrespective of the molar ratio used. Only three 1 : 3 complexes could be prepared (**12**,**23**,**25**). It seems that for a given metal ion the nature of the anion present also affects the product identity. The direct isolation of **23**, which has the $[Cu(APH)_3]^{2+}$ cation, is attributed to the poor coordinating ability of BF_4^-.

It is well established [5,13] that Ni(II) salts form, in general, all the 1 : 1, 1 : 2 and 1 : 3 series of complexes with a given chelating bidentate neutral ligand with aliphatic N-donor atoms provided that there are no steric effects. Also 2-pyridinal hydrazone readily forms tris-complexes with bivalent metal ions [13]. The tendency of APH to form mainly 1 : 1 and 1 : 2 complexes can be attributed to the presence of the methyl group which together with the very definite steric requirements of the hydrazone grouping when coordinated, lead to inter-ligand repulsion [13]. The Pauling Electroneutrality Principle can also provide another reasonable explanation for the failure to isolate many 1 : 3 complexes with Mn(II), Fe(III), Ni(II) and Cu(II). With the strongly basic APH ligand a large transfer of charge to the central atom is possible, and a relatively small number of APH ligands is needed to bring about “electroneutrality”, especially in the presence of other less basic anionic ligands, e.g. Cl^-, Br^-, NO_3^- and NCS^- [14].

TABLE 1

Preparative data, colours and molar conductivity values for the complexes prepared

Compound number	Complex	Metal salt: ligand [a]	Yield (%)	Colour	Λ_M [g,h] (S cm^2 mol^{-1})
1	Mn(APH)Cl_2	1.42 : 1, 1.16 : 1, 1.07 : 1	81 [e]	pale yellow	41
2	Mn$(APH)_2Cl_2$	1 : 2.33, 1 : 2.60, 1 : 3.57	75 [f]	yellow	68
3	Mn(APH)Br_2	1.20 : 1, 1.08 : 1	80 [e]	yellow	75
4	Mn$(APH)_2Br_2$	1 : 2.33, 1 : 2.70, 1 : 4.06	76 [f]	yellow	65
5	Mn$(APH)_2(NO_3)_2$	1.33 : 1, 1.03 : 1, 1 : 2.20, 1:3.49	78	yellow	57
6	Fe(APH)Cl_3	1.62 : 1 ,1.05 : 1	80 [e]	brick red	45
7	Fe$(APH)_2Cl_3$	1 : 2.06, 1:3.20, 1 : 4.17	65 [f]	dark brown	50
8	Ni(APH)Cl_2	2.09 : 1 ,1.30:1,1.04:1	92 [e]	pale green	44
9	Ni$(APH)_2Cl_2$	1:2.30, 1 : 2.71, 1 : 3.26, 1 : 4.15	83 [f]	pale olive green	44
10	Ni(APH)Br_2	2.17 : 1, 1.30 : 1, 1.09 : 1	88 [e]	pale green	42
11	Ni$(APH)_2Br_2$	1 : 2.31, 1 : 2.64, 1 : 2.80	44 [f]	pale olive green	72
12	Ni$(APH)_3Br_2$	1 : 3.20, 1 : 4.17	80 [f]	beige-pink	64
13 [b]	Ni$(APH)_2(NO_3)_2$	1 : 2.30, 1 : 3.34	40 [f]	pale olive green	75
14	Ni(APH)$(NCS)_2$	2.13 : 1, 1.30 : 1	61 [e]	pale olive green	59
15	Ni$(APH)_2(NCS)_2$	1 : 2.30, 1 : 3.47	60 [f]	beige-pink	64
16	Cu(APH)Cl_2	1.46 : 1, 1.30 : 1	83 [e]	pale green	25
17	Cu$(APH)_2Cl_2$	1 : 2.31, 1 : 3.30	66 [f]	dark green	47

18	$Cu(APH)Br_2$	1.57 : 1, 1.30 : 1	60 [e]	brownish green	39
19	$Cu(APH)_2Br_2$	1 : 2.31, 1 : 2.60, 1 : 3.30	65 [f]	dark green	37
20	$Cu(APH)(NO_3)_2$	1.30 : 1, 1.17 : 1	45 [e]	green	68
21	$Cu(APH)_2(NO_3)_2$	1 : 2.31, 1 : 3.19, 1 : 4.40	50 [f]	dark olive green	66
22	$Cu(APH)(CH_3COO)_2$	1.37 : 1, 1.07 : 1, 1 : 1.57, 1 : 2.03	30	pale green	1
23 [c]	$Cu(APH)_3(BF_4)_2$	1 : 2.17, 1 : 2.71, 1 : 3.21, 1 : 4.01	30 [f]	green	71
24 [d]	$Cu(APH)_2SO_4$	1 : 1.91, 1 : 2.06	70 [f]	dark green	13
25	$Cu(APH)_3SO_4$	1 : 3.51, 1 : 4.00	65 [f]	brown	31
26	$Cd(APH)Br_2$	1.20 : 1, 1 : 1.51, 1 : 2.25, 1 : 3.17	90	white	20
27	$Cd(APH)I_2$	1.20 : 1	80 [e]	white	38
28	$Cd(APH)_2I_2$	1 : 2.25, 1 : 3.40, 1 : 4.21	82 [f]	white	37
29	$Cd(APH)(NO_3)_2$	1.20 : 1	30 [e]	white	77
30	$Cd(APH)_2(NO_3)_2$	1 : 2.25, 1 : 3.43	85 [f]	pale orange	44
31	$Hg(APH)Cl_2$	2.01 : 1, 1.22 : 1, 1 : 2.00, 1 : 3.17	80	white	2
32	$Hg(APH)Br_2$	1.99 : 1, 1 : 2.33, 1 : 3.40	81	white	2

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[a] Molar ratio.

[b] $Ni(APH)(NO_3)_2$ could not be prepared in pure form.

[c] Using metal salt: APH molar ratios lower than 1:2, e.g. 1:1.45, solids with poor analytical results were isolated.

[d] Using a 1 : 1 metal salt: APH molar ratio a solid with poor analytical results was obtained.

[e] Based on the ligand.

[f] Based on the metal.

[g] Values of molar conductivity for about 10^{-3} M solutions in DMSO.

[h] The conductivities of most solutions change with time.

Physical properties of the complexes

Yields, colours and molar conductivity values are also given in Table 1. All the complexes gave excellent analytical results for M, X (X = Cl, Br, I, NCS), C, H and N. The complexes are polycrystalline or powder-like, stable in atmospheric conditions and readily soluble only in DMF and DMSO, frequently with colour changes; however, the 1 : 2 and 1 : 3 complexes have a moderate solubility in nitromethane. Only the Λ_M values of **22**, **31** and **32** in DMSO are in accord with these complexes being formulated as non-electrolytes [15]. The Λ_M values of the other complexes indicate ionization [15]. However, the facts that the conductivities of the solutions change with time, and that the solution and solid state *d–d* spectra of the Mn(II), Fe(III), Ni(II) and Cu(II) species differ, can be attributed to the strong donor capacity of DMSO, which frequently leads to displacement of anionic ligands and change of electrolyte type [15]. The Λ_M values of **12** and **23**, which are formulated as cationic $[M(APH)_3]^{2+}$ complexes, indicate 1 : 2 electrolytes [15], while **25** formulated as $[Cu(APH)_3]^{2+}SO_4^{2-}$ appears to be an 1 : 1 electrolyte in DMSO [15].

X-ray powder diffraction patterns indicate that each compound represents a definite complex, not merely mixtures of other stoichiometric types or starting materials. The data also indicate the formation of four pairs of isomorphous compounds; the first pair includes the complexes **2** and **4**, the second the complexes **8** and **10**, the third the complexes **9** and **11** and the fourth includes the compounds **31** and **32**. The pattern of **1** resembles that of **3**, but the two complexes are not exactly isostructural. It is worth noting that the X-ray powder pattern of **26** is completely different from that of **27**. The small number of diffraction lines observed for **1**, **3**, **8**, **10**, **14**, **26**, **31** and **32** may suggest polynuclear arrangements [16]. Because of the insolubility of the prepared complexes in suitable solvents, we were unable to obtain samples for single-crystal X-ray structural studies.

Infrared spectra

The principal IR bands of interest are listed in Table 2. The significant changes in the ligand bands upon complexing are the increases in υ(C=N), ν(N–N) and δ(Py) (in **22** the characteristic in-plane deformation band of the pyridine ring does not shift) and the absence of large systematic shifts of the $\nu_{as}(NH_2)$, $\nu_s(NH_2)$ and $\delta(NH_2)$ modes to lower frequencies. These data indicate coordination through nitrogens of the azomethine group (N^1) [2,6,9,10] and pyridine ring [17], and no interaction between the terminal amino nitrogen (N^2) and the metal ions. We thus believe APH to belong to the class of chelating ligands containing the –N=C–C=N– grouping.

The IR spectra of **14** and **15** exhibit ν(CN), ν(CS) and δ(NCS) modes in the regions characteristic of bridging thiocyanates and terminal N-bonded isothiocyanate groups respectively [18]. In the spectra of **5**, **13**, **21** and **30**, the vibrational fundamentals of the nitrato groups are strongly indicative of the presence of monodentate nitrates, because the separation of the two highest frequency bands, shown in Table 2, is lower than 150 cm^{-1} [18,19]. The complexes **20** and **29** seem to contain two chelated bidentate nitrato groups, as the above separation is 212 and 180 cm^{-1} respectively [18,19]. The possibility of bridging nitrato groups is ruled out, because the highest frequency nitrato mode appears below 1550 cm^{-1} [20]; also the absence of a single strong band in the 1350–1400 cm^{-1} region confirms that ionic D_{3h} nitrates are absent [20]. The frequencies of the ν_3 and ν_4 BF_4^- modes in the spectrum of **23** are indicative of non-coordinated tetrafluoroborate anions [18]. The number and the frequencies of the S–O stretching bands in the spectrum of **24** are indicative of the presence of a bidentate chelating C_{2v} sulphato ligand [18,19], while in the spectrum of **25** indicate an ionic T_d sulphate group [18,19]. The frequencies of the $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$ bands in **22** indicate symmetrically bridging acetate groups [21].

The number and the frequencies of the ν(MX) far-IR bands (X = Cl, Br, NCS, ONO_2) fully support [2,3,6,8–11,16,17–19,22–26] the proposed structures of the complexes (see Conclusions). The far-IR spectra of **16**, **18** and **27** show the two ν(M–X) bands in the region expected for pseudo-tetrahedral monomeric stereochemistry. A medium to strong M- and X-sensitive band at a frequency lower than 295 cm^{-1} in the spectra of **2**, **5**, **9**, **13**, **15**, **21** and **30** arises from the $\nu(M{-}X)_t$ vibration in a monomeric *trans* octahedral structure, while the two $\nu(M{-}X)_t$ bands in **17**, **20** and **29** indicate a *cis* octahedral structure. The far-IR spectrum of **6** is indicative of the presence of both terminal and bridging Fe(III)–Cl bonds, suggesting a dimeric or polymeric structure. The formulation $[Fe(APH)_2Cl_2]^+[FeCl_4]^-$ can be ruled out because the strong IR-active ν_3 stretching Fe–Cl band of the tetrahedral $[FeCl_4]^-$ ion is not observed around 370 cm^{-1}. A monomeric 5-coordinate $[Fe(APH)Cl_3]$ species (C_s or C_{2v} point group) can also be ruled out because such a structure should imply three $\nu(Fe{-}Cl)_t$ vibrations. For **7**, the complicated far-IR spectrum and the uncertainty about the positions of the Fe–N vibrations prohibited a detailed analysis. The far-IR spectrum of **28** exhibits no bands attributable to Cd–I stretching modes. The far-IR spectra of **26**, **31** and **32** seem incompatible with a monomeric skeleton, but they can be explained on the basis of polymeric halide-bridged structural units while the complexes still contain terminal M–X bonds. The three $\nu(CdBr)_b$ bands observed in **26** may suggest that this complex has the same structure as $Cd(dmpd)Br_2$ (dmpd = 2,2-dimethylpropane-1,3-diamine) [22], where a N_2CdBr_4 skeleton exists formed by the two nitrogen atoms, one terminal bromine atom and three bridging bromine atoms shared among three metal atoms. If an idealized C_s symmetry is assumed, three $\nu(CdBr)_b$ bands at frequencies lower than 170 cm^{-1} and one $\nu(Cd{-}Br)_t$ in the 200–180 cm^{-1} spectral range are expected. These bands are observed in **26**.

TABLE 2

Diagnostic infrared data (cm^{-1}) of 2-acetylpyridine hydrazone and its metal complexes

Comp.	$\nu(C{=}N_2)$ (+ring stretch vibration)	$\nu(N{-}N)$	Ring deformation bands		Anion bands [b]						Far-IR bands [g,h]	
			in-plane	out-of-plane	$\nu(CN)$	$\nu(CS)$	$\delta(NCS)$	$\nu_1(A_1)$	$\nu_4(B_2)$ (+ring stretch vibr.)	$\nu_4(B_2)$	$\nu(M{-}X)_t$	$\nu(MX)_b$
APH	1569s[a]	1135s	620m	402m								
1	1602s	1173s	642m	418m								< 220
2	1608vs	1164vs	638m	412m							222s	
3	1596vs	1163s	638m	416m								< 220
4	1608vs	1170s	640m	415m							< 200	
5	1601vs	1170sb	639m	410m				1298m	1435ms		255s	
6	1573m[a]	1169m	652m	430m							323vsb	235m
7	1572m[a]	1165m	648m	430m							n.a.	n.a.
8	1591vs	1169vs	642m	425m								< 220
9	1593vs	1153m	641m	419m							225s	
10	1590vs	1168vs	641m	420m								< 220
11	1592vs	1152m	641m	419m							< 220	
12	1595vs	1163s	633m	414m								
13	1596vs	1158m	641w	413w				1317s	1420s		271m	
14	1579m	1159m	641m	419m	2110vs, 2102vs	777vs	430m					243m
15	1590vs	1155s	640m	418m	2070vs	obs.	469m				264m	
16	1591vs	1162s	646m	412m							301vs, 278m	
17	1592vs	1161m	639m	405w							267m, 244m	
18	1580sh[a]	1159s	644m	412m							260m, 242m	

19	1592vs	1160m	640w	404w					< 220
20	1575m[a]	1180s	648m	412m	1500s		1288s	322m, 296m	
21	1592s	1153m	640m	408m	1320m	1422s		295m	
22[c]	1612vs	1153m	621m	n.o.				n.a.	
23[d]	1600vs	1167m	643w	417m					
24[e]	1598s	1160sh	633m	410w				n.a.	
25[f]	1595m	1157sh	635w	407w					
26	1584vs	1162m	637m	452w				195s	153mb, 145m, 137m
27	1588vs	1155s	637m	438m				163m, 147s	
28	1584vs	1157s	632m	452m					
29	1589s	1169m	639m	452w	1465s		1285m	243s, 219m	
30	1591vs	1162m	635m	651m	1303m	1426s		228s	
31	1591s[a]	1165s	633m	452m				271s	177sb
32	1592vs	1163s	635m	451w				201s	123sb

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[a] Pure $\nu(C{=}N_2)$ vibration.

[b] The IR spectra of **5**, **13**, **21**, **29** and **30** in Nujol or hexachlorobutadiene and of their powdered KBr pellets differ in the regions of nitrato absorptions; the obtained spectra in KBr are indicative of the simultaneous presence of ionic D_{3h} nitrates and coordinated nitrato groups.

[c] $\nu_{as}(COO^-)$ at 1620(vs) and $\nu_s(COO^-)$ (+ring stretch vibr.) at 1427(vsb) cm^{-1}.

[d] $\nu_3(BF_4^-)$ at 1050(vsb) and $\nu_4(BF_4^-)$ at 525(m) cm^{-1}.

[e] $\nu_3(SO_4^{2-})$ at 1235(m), 1115(vs), 1025(s) and $\nu_1(SO_4^{2-})$ at 936(m) cm^{-1}.

[f] The ν_3 mode of the uncoordinated T_d SO_4^{2-} ion appears at 1112(s) cm^{-1}.

[g] Only for the Cd(II) and Hg(II) complexes are there data in the 220–50 cm^{-1} region.

[h] Assignments of $\nu(MX)$ bands have been made by noting (i) the frequencies of internal modes of APH, (ii) bands principally dependent on X, (iii) the variation in band frequency with changing metal ion, and (iv) extensive literature reports.

s = strong; vs = very strong; m = medium; w = weak; b = broad; sh = shoulder; n.o. = not observed; n.a. = not assigned; obs. = obscured by strong bands of coordinated APH; M = metal; X = Cl, Br, NCS, ONO_2, OSO_3, $OOCCH_3$; $\nu(M{-}X)_t$ is the stretching vibration of the terminal M–X bond; $\nu(MX)_b$ is the stretching vibration of the M–X bond in the bridging MXM group.

Nuclear magnetic resonance spectra

Table 3 gives the diagnostic ^1H NMR chemical shifts of APH and its diamagnetic complexes in d_6-DMSO (downfield from TMS). The study was based on comparisons with a number of related hydrazone ligands and complexes [6,27] and on deuterium exchange experiments. In the spectra of the diamagnetic complexes the $-NH_2$ signal undergoes only a marginal shift to indicate the ion-involvement of the terminal amino nitrogen in coordination; a large downfield shift would be expected if coordination had occurred [16].

The spectra of **26**–**32** show a small downfield shift of the methyl and 6-pyridyl protons, compared to the corresponding signals in the free ligand; this fact supports the coordination of azomethine and ring nitrogen atoms to Cd(II) and Hg(II) [28]. NMR evidences for hydrazo–azo tautomeric structures were not found [27].

Magnetochemical and ligand field spectral studies

Table 4 gives the room temperature magnetic moments and details of the solid state (diffuse reflectance) spectra of the prepared complexes. The μ_{eff} values of the Mn(II), Fe(III) and Ni(II) complexes show that these are all high spin; the small orbital contribution in the $t_{2g}^6e_g^2$ Ni(II) case indicates six-coordinate structures [29]. The electronic spectra of the Mn(II), Fe(III) and Ni(II) complexes can also be assigned to d–d transitions in pseudo-octahedral structures [29,30]. The band positions and $10Dq$ values in the Ni(II) complexes indicate [30,31] that the ligand field changes from N_2X_4 in **8** and **10** to N_4X_2 in **9**, **11** and **13**, and to N_6 in **12** and **15** ($X = Cl, Br, ONO_2$).

TABLE 3

Diagnostic ^1H NMR data (δ, ppm) [a] of APH and its diamagnetic complexes in d_6-DMSO

Complex	$-CH_3$	$-NH_2$	H_6
APH	2.13s	6.83sb	8.45d
26	2.24s	7.10sb [b]	8.57d
27	2.25s	7.02sb [b]	8.58d
28	2.22s	6.94sb	8.52d
29	2.27s	7.03sb [b]	8.58d
30	2.22s	6.90sb	8.58d
31	2.23s	7.28sb [b]	8.54d
32	2.25s	7.37sb [b]	8.53d

[a] The spectra were run approximately 1 h after dissolution.

[b] If the spectra are run immediately after dissolution this signal is slightly shifted upfield.

s = singlet; d = doublet; b = broad.

The room temperature μ_{eff} values indicate that the Cu(II) complexes prepared, except **22**, are magnetically dilute. The d–d spectra of **16** and **18** are indicative of pseudo-tetrahedral stereochemistry [16,30,32]. The proposed pseudo-tetrahedral stereochemistry is further supported by their large μ_{eff} values [32]. The d–d spectra of **17**, **19**, **20**, **21** and **23**–**25** are fairly typical of distorted six-coordinate Cu(II) complexes [30]. Although the complexes **23** and **25** seem to contain the same chromophore (CuN_6), they exhibit different d–d spectra at room temperature. This is due to the fact that the factors which determine structure in Cu(II) chemistry can be very subtle and certainly include crystal lattice forces, so that a given cationic, for example $[Cu(APH)_3]^{2+}$, or anionic species may have a structure or a degree of distortion which is variable and depends on the counter ion [30]. The electronic spectrum of **22**, in both d–d and CT regions, is characteristic of copper(II) acetate dimers of the $Cu_2(CH_3COO)_4L_2$ type, where L is a monodentate N-donor ligand [33].

Electron spin resonance spectra

ESR data for the Cu(II) complexes obtained from powdered samples are presented in Table 5. The g values of **16** and **18** are in the range reported for flattened pseudo-tetrahedral Cu(II) complexes [34]. The spectra of **17** and **25** are rhombic in character, exhibiting three clearly resolved peaks. The calculated R values indicate a d_{z^2} ground state for **17** and suggest $d_{x^2-y^2}$ for **25** [7,35]. The lowest g value of **17** is very close to 2.00; this may suggest a compressed rhombic octahedral stereochemistry [35,36]. The X-band room temperature polycrystalline ESR spectra of **20**, **21**, **23** and **24** are typical of those reported for axial type Cu(II) complexes, with two g values $g_{\parallel} > g_{\perp} > 2.00$, suggesting a $d_{x^2-y^2}$ (or d_{xy}) ground state and consistent with elongated tetragonal octahedral stereochemistries [7,36]. The calculated G values lie in the 4.6–5.2 region and, thus, the extent of interaction between Cu(II) centres is negligible [37]. The ESR spectrum obtained for **19** is quite different from that normally observed for tetragonally distorted octahedral Cu(II) complexes. Indeed, an axial "reversed" spectrum was observed with $g_{\perp} > g_{\parallel}$. Two possibilities exist [38]. One is that the single-ion electronic ground state of the Cu(II) ions is largely d_{z^2}; the other possibility is that the single-ion ground state is largely $d_{x^2-y^2}$ and the observed resonance is due to sites which are not equivalent within the unit cell and misalignment of the tetragonal axes. Because powder spectra can only yield information about the crystal g tensors [38] and as the molecular structure of **19** is not known, an additional analysis of the observed "reversed" spectrum is not possible.

We observed no transitions in the $M = 2$ region of the spectra (i.e. at about 1600G) for any of the complexes discussed above. Thus, binuclear structures can be ruled out [35,36]. The X-band ESR spectrum of **22**, not

TABLE 4

Solid state magnetic moments and electronic spectral data in the 29400–11230 cm^{-1} region for the Mn(II), Fe(III), Ni(II) and Cu(II) complexes of 2-acetylpyridine hydrazone

Complex	μ_{eff} [a,b] (BM)	Solid state [b] electronic (diffuse reflectance) spectra (10^3 cm^{-1})							
Octahedral Mn(II) complexes		$^6A_{1g} \rightarrow {}^4E_g(D)$	$^6A_{1g} \rightarrow {}^4T_{2g}(D)$	$^6A_{1g} \rightarrow {}^4T_{2g}(G)$	$^6A_{1g} \rightarrow {}^4T_{1g}(G)$				
1	6.06	28.99	26.53sh	21.28	18.52sh				
2	5.91	28.01		20.92					
3	5.85			21.74sh	15.80sh				
4	5.76			21.60	15.81sh				
5	6.05	28.90		20.70sh	15.55sh				
Octahedral Fe(III) complexes		LMCT	$^6A_{1g} \rightarrow {}^4T_{2g}(D)$	$^6A_{1g} \rightarrow {}^4A_{1g}, {}^4E_g(G)$	$^6A_{1g} \rightarrow {}^4T_{2g}(G)$	$^6A_{1g} \rightarrow {}^4T_{1g}(G)$			
6	5.97	22.88	27.78	24.81	20.41sh	12.00			
7	5.71	23.26	27.02	24.85	20.40				
Octahedral Ni(II) complexes		$^3A_{2g} \rightarrow {}^3T_{1g}(P)$	$^3A_{2g} \rightarrow {}^1T_{2g}$ [d]	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	$^3A_{2g} \rightarrow {}^1E_g$ [d]	$^3A_{2g} \rightarrow {}^3T_{2g}$	$10Dq$ (cm^{-1})	B (cm^{-1})	β
8	3.30	25.00		13.89		[c]	8360	929	0.90
9	3.14	28.17	18.52sh	16.95		[c]	10460	918	0.89
10	3.18	25.06	20.70sh	14.26		[c]	8590	905	0.88
11	3.16	27.78	19.05sh	16.81		[c]	10415	890	0.86

12	3.08	28.98	20.31		12.51	12510	719	0.70
13	3.36	28.74	17.70	12.90sh	[c]	11050	884	0.86
14	3.10	29.00	17.45		[c]	10730	942	0.91
15	3.18	28.24	18.87		12.12, 11.69	11905	735	0.71
Cu(II) complexes		LMCT	d–d	Other bands				
16	2.61	27.78, 25.00sh	14.92sh, 12.99, 12.12sh					
17	1.88	27.47, 24.09sh	13.42					
18	2.06	27.40sh, 20.62, 19.80	14.81, 13.70, 12.19					
19	1.90	26.67, 25.10sh, 20.83	12.82					
20	1.93	29.41	13.80					
21	1.83	28.17	15.50					
22	1.57	26.67	13.99					
23	1.91		15.49	28.95, 27.03sh				
24	1.86	27.03, 24.69	14.49					
25	2.07		18.96, 15.04	25.97				

[a] Per metal ion.

[b] Measured at room temperature.

[c] Below the lowest energy limit of the instrument used.

[d] Spin-forbidden bands frequently observed in octahedral Ni(II) complexes.

LMCT = ligand-to-metal charge transfer; sh = shoulder.

TABLE 5

X-band room temperature ESR data for the polycrystalline Cu(II) complexes of 2-acetylpyridine hydrazone

Complex	g_1	$g_\perp$	g_2	$g_\parallel$	g_3	$\langle g \rangle$[a]	G[b]	R[c]
16		2.020		2.130		2.056		
18		2.031		2.153		2.071		
17	2.017		2.199		2.284	2.167		2.14
25	2.060		2.183		2.274	2.172		1.35
19		2.157		2.041		2.118		
20		2.042		2.201		2.095	4.79	
21		2.038		2.196		2.091	5.16	
23		2.065		2.299		2.143	4.60	
24		2.053		2.245		2.117	4.62	

[a] $\langle g \rangle = \frac{1}{3}g_\parallel + \frac{2}{3}g_\perp$ or $\frac{1}{3}(g_1 + g_2 + g_3)$.

[b] $G = \dfrac{g_\parallel - 2}{g_\perp - 2}$.

[c] $R = \dfrac{g_2 - g_1}{g_3 - g_2}$.

included in Table 5, is very similar to those of $[Cu(CH_3COO)_2(H_2O)]_2$ and $[Cu(CH_3COO)_2L]_2$ [33,39], where L is a monodentate N-donor ligand, thus confirming that this complex has an acetate-type binuclear structure with axial symmetry. The absorption at 1600G is assigned to the $\Delta M_s = \pm 2$ in the copper(II) dimer.

Thermal studies

The thermal decomposition of the prepared complexes was also studied using mainly TG/DTG techniques. The data for the Mn(II), Fe(III), Cu(II), Cd(II) and Hg(II) compounds present no special interest as their decomposition is characterized by rather complex degradation mechanisms; all the complexes decompose without the formation of stable intermediates, as no stoichiometric compounds can be assigned to the curves' inflections. CAUTION: complex **20** explodes violently at around 135 ° C.

Some of the Ni(II) complexes of APH decompose via stable intermediates. Data are presented in Table 6. The TG and DTG curves of **9** show a first mass loss between 250 and 297 ° C, which exactly corresponds to the release of one ligand molecule. The IR and d–d spectra, the μ_{eff} value and the X-ray powder pattern of the product obtained after a TG experiment up to 300 ° C (**9a**) are exactly the same as the corresponding data for complex **8** isolated by synthetic procedures. The DTA profile for the transformation of bis → mono species, being an endotherm followed by an exotherm, suggests that the decomposition may take place with geometrical isomerization [41]. A clear plateau is not reached above 300 ° C, because a new decomposition starts immediately. There is a second very distinct inflection in the TG curve

TABLE 6

Thermal decomposition data [a] for the Ni(II) complexes of APH

Decomposition reaction	Temperature range (°C)	E_a [c] (kJ mol^{-1})
$Ni(APH)Cl_2$ (**8**) → $Ni(APH)_{0.5}Cl_2$ (**8a**)	300–335	
$Ni(APH)_{0.5}Cl_2$ (**8a**) → NiO	375–537	[d]
$Ni(APH)_2Cl_2$ (**9**) → $Ni(APH)Cl_2$ (**9a**)	250–297	
$Ni(APH)Cl_2$ (**9a**) → $Ni(APH)_{0.5}Cl_2$ (**9b**)	300–337	[d]
$Ni(APH)_{0.5}Cl_2$ (**9b**) → NiO	380–551	
$Ni(APH)Br_2$ (**10**) → $Ni(APH)_{0.5}Br_2$ (**10a**)	285–332	
$Ni(APH)_{0.5}Br_2$ (**10a**) → NiO	373–572	[d]
$Ni(APH)_2Br_2$ (**11**) → $Ni(APH)Br_2$ (**11a**)	279–307	
$Ni(APH)Br_2$ (**11a**) → $Ni(APH)_{0.5}Br_2$ (**11b**)	308–336	[d]
$Ni(APH)_{0.5}Br_2$ (**11b**) → NiO [b]	381–569	
$Ni(APH)_3Br_2$ (**12**) → $Ni(APH)_2Br_2$ (**12a**) [b]	220–260	
$Ni(APH)_2Br_2$ (**12a**) → $Ni(APH)Br_2$ (**12b**)	285–321	[d]
$Ni(APH)Br_2$ (**12b**) → NiO [b]	390–626	
$Ni(APH)(NCS)_2$ (**14**) → $Ni(NCS)_2$	275–330	122
$Ni(APH)_2(NCS)_2$ (**15**) → $Ni(APH)(NCS)_2$ (**15a**)	225–271	98
$Ni(APH)(NCS)_2$ (**15a**) → $Ni(NCS)_2$	280–328	128

[a] Based on TG/DTG data.

[b] These decompositions occur in two steps.

[c] Determined as described in ref. 40.

[d] No data available.

From the overall study it is concluded that from a structural point of view **8** = **9a**, **8a** = **9b**, **10a** = **11b**, **11** = **12a**, **14** = **15a**, but **10** ≠ **12b** (see also text).

between 300 and 337°C. The weight loss in this step corresponds very well with the formation of $Ni(APH)_{0.5}Cl_2$. A plateau is reached at about 340 up to 370°C. The product obtained after a TG experiment up to 350°C (**9b**) was isolated. It has the same spectroscopic (IR, d–d) and magnetochemical characteristics as those of the analogous product (**8a**) obtained from the thermal decomposition of **8**; **8a** could also be isolated. The magnetochemical ($\mu_{eff} = 3.80$ BM at 17°C) and spectral d–d ($10Dq = 4310$ cm^{-1}) and far-IR (ν(Ni–Cl)$_t$ at 296 cm^{-1} and ν(NiCl)$_b$ at 207 cm^{-1}) data indicate pseudo-tetrahedral stereochemistry with both terminal and bridging chlorides. The last curve inflection of **9** gives a final plateau above 550°C corresponding to the formation of NiO. The probable decomposition mechanism of **9** is shown in Fig. 1. Similar mechanistic paths have been proposed for the thermal decomposition of Ni(II) complexes with bidentate N-donor ligands [41,42]. Completely analogous thermal data were obtained for the pair of 1 : 2 and 1 : 1 bromo complexes **11** and **10**. It is a matter of interest that the intense blue hemi-species $Ni(APH)_{0.5}X_2$ (X = Cl, Br) have been isolated in pure form from solid-state reactions, whilst attempts for their preparation from solution have been unsuccessful (see Table 1).

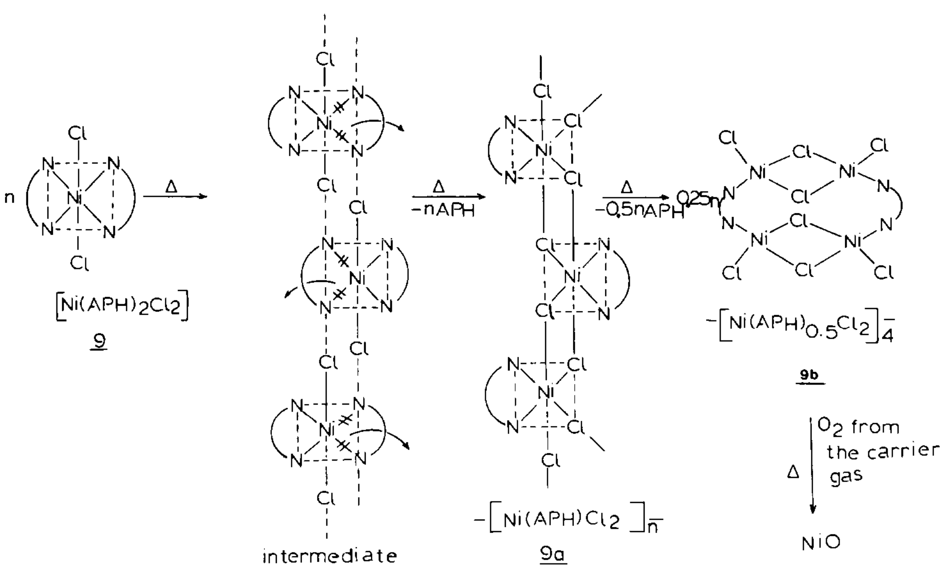


Fig. 1. The thermal decomposition of $Ni(APH)_2Cl_2$ (**9**).

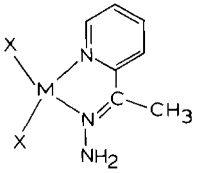
The TG and DTG curves of **12** show a first mass loss in two steps between 220 and 260 °C, which corresponds to the release of one ligand molecule. A plateau is reached at 265 °C up to 282 °C. The stable intermediate **12a** was isolated by the temperature arrest technique in nitrogen atmosphere. The magnetic, spectral and powder X-ray data of **12a** are the same as the corresponding data of **11** isolated by the synthetic procedure. There is a second very distinct inflection in the TG curve between 285 and 321 °C. The weight loss in this step corresponds to the formation of a product with the formula $Ni(APH)Br_2$. A plateau is reached at 325 °C up to about 385 °C. The product isolated after a TG experiment up to 340 °C (**12b**) has different magnetic, spectral and powder X-ray diffraction characteristics compared with those of **10**, which was isolated by synthesis. This indicates that the two solids with the $Ni(APH)Br_2$ formula (**10**,**12b**) have different structures. It is worth noting, however, that the two solids **10** and **12b** have d–d spectra and μ_{eff} values characteristic of octahedral environments around Ni(II). The product **12b** starts to decompose at 390 °C and transforms into NiO at 626 °C in two steps through a stable (between 418 and 485 °C) non-stoichiometric intermediate.

The mono ligand complex **14** starts to decompose at 275 °C and transforms into $Ni(NCS)_2$ at 330 °C, possibly through an unstable non-isolable intermediate $Ni(APH)_{0.5}(NCS)_2$ as is indicated by a poorly resolved inflection at 305 °C in the TG curve; this inflection is not clearly seen in the TG curve of **15**. The complex **15** is converted into $Ni(NCS)_2$ in two steps via the formation of $Ni(APH)(NCS)_2$. This intermediate was unstable; however, it could be isolated at about 275 °C by keeping the rate of heating at 1 °C min^{-1}. The isolated solid (**15a**) has the same magnetic and spectral characteristics as those of **14**. Similar decomposition processes have been observed with diamine complexes of nickel(II) thiocyanate [5,43]. Finally, the complex **13** decomposes without the formation of stable intermediates; so, the 1 : 1 nitrate complex, which was not isolated by synthesis, cannot be prepared from the 1 : 2 complex by thermal decomposition.

CONCLUSIONS

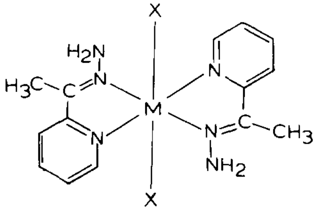
From the overall study presented above, it is concluded that in all the new complexes prepared, except **22**, APH behaves as a bidentate chelate ligand bonding through both the pyridine and methine (N^1) nitrogen atoms. The N^1 coordination is the usual bonding mode of hydrazone ligands to metals; coordination from N^2 is known to occur when very bulky substituents occur on the iminic carbon atom [44]. In **22** the ligand exhibits a monodentate behaviour, the bonding site being N^1.

Several stereochemistries are assigned for the APH complexes in the solid state. The tetrahedral complexes **16**, **18** and **27** are believed to have the following structure:

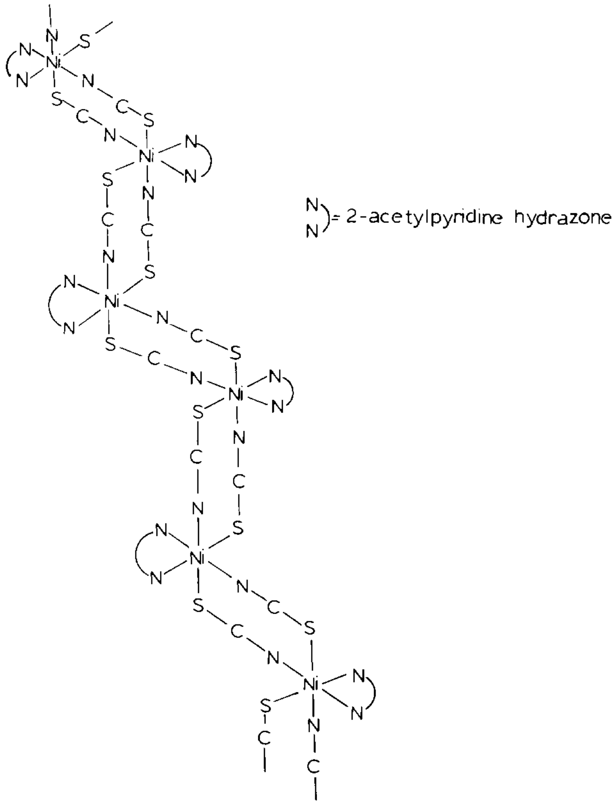


16, 18, 27

Synthetic and spectroscopic data suggest that **28** consists of the monomeric pseudo-tetrahedral CdN_2N_2 entity formed by two chelating APH ligands without coordination of the iodide ions. The complexes, **2**, **4**, **5**, **9**, **11**, **13**, **15**, **21** and **30** are almost certainly neutral bis-chelates; the monomeric *trans*-octahedral structural type shown below



2, 4, 5, 9, 11, 13, 15, 21, 30 ; M = Mn, Ni, Cu, Cd; X = Cl, Br, ONO2, NCS is assigned for them. All data for **12** and **23** suggest a monomeric *cis*-octahedral stereochemistry with a MN_6 chromophore (M = Ni, Cu); **23**, although *cis*-octahedral, appears to have a *trans* elongated distortion [45]. The compounds **17** and **25** have monomeric six-coordinate rhombic geometries with *cis*-CuN_4Cl_2 and *cis*-CuN_6 chromophores respectively. The complex ions $[Cu(APH)_3]^{2+}$ of **23** and **25** are probably distortion isomers [36]. Monomeric *cis*-octahedral stereochemistries with N_2O_4 (**20**,**29**) and N_4O_2 (**24**) environments are proposed for **20**, **24** and **29**; the Cu(II) complexes appear to be axially elongated. For **22**, a dimeric structure is assigned with two Cu(II) atoms bridged in pairs by four acetato groups to form a binuclear molecule, similar to that found in copper(II) acetate monohydrate [46], the oxygen of water being replaced here by the methine nitrogen of monodentate APH at the apical position of the coordination polyhedron. The complex **6** has a dimeric or polymeric pseudo-octahedral structure with the presence of both terminal and bridging chlorides. The d–d spectrum of

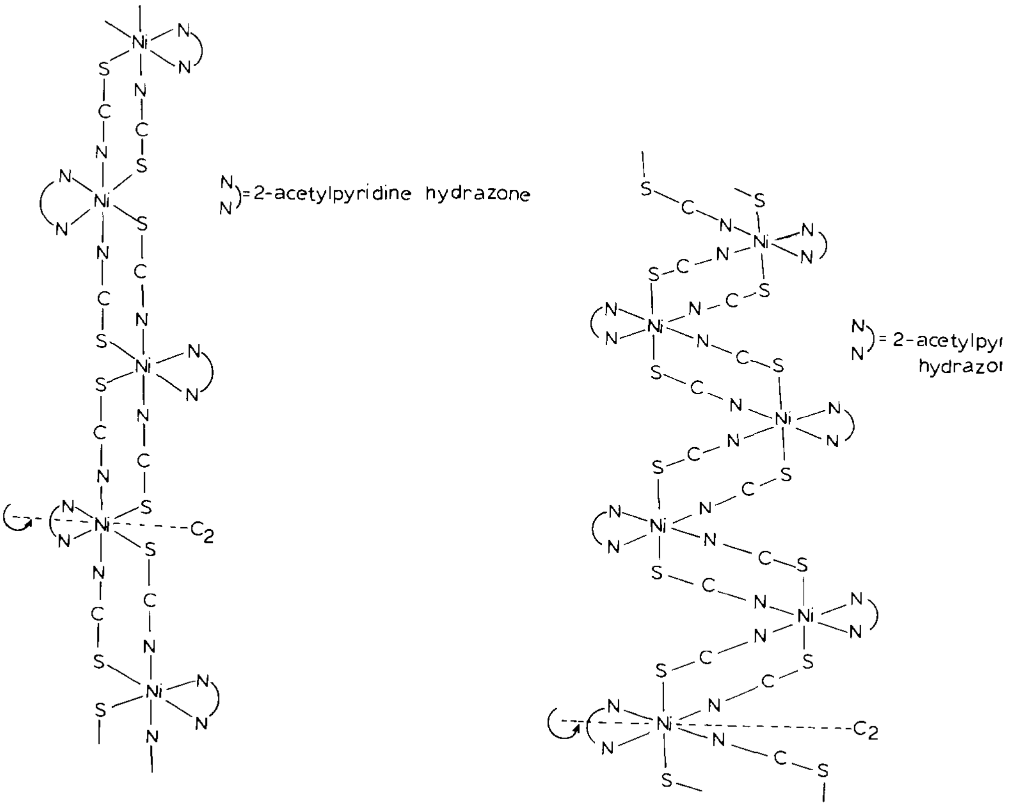


cis-thiocyanate-N, cis-thiocyanate-S

Scheme 1.

the dark brown complex **7** is indicative of an octahedral stereochemistry but its confused far-IR spectral region did not allow us to assign a more specific structural type. Polymeric octahedral structures are proposed for **1**, **3**, **8**, **10**, **14**, **26**, **31** and **32** formed by chelating APH molecules and exclusively bridging (**1**, **3**, **8**, **10**, **14**) or simultaneously bridging and terminal (**26**, **31**, **32**) anionic ligands.

We comment further on the possible structure of Ni(APH)(NCS)$_2$ (**14**), because thiocyanate-bridged transition-metal octahedral polymers of the type ML(NCS)$_2$, where L is bidentate chelating N-donor ligand, exhibit very interesting and quite variable magnetic-exchange behaviour [47]. Our studies by optical and IR spectroscopy, as well as by the μ_{eff} value at room temperature, indicated that **14** is a polymer with six-coordinate metal centres and bridging thiocyanate ions. So, structures consisting of (a) discrete molecules of Ni(APH)(NCS)$_2$, i.e. a four-coordinate Ni(II) monomer, either



trans- thiocyanate-N, cis- thiocyanate-S

cis- thiocyanate-N, trans- thiocyanate-S

Scheme 2.

square planar or more likely pseudo-tetrahedral, or (b) discrete dimers containing pairs of five-coordinate Ni(II) centres resulting from both bridging and terminal thiocyanates, i.e. a dimer [(APH)(SCN)Ni(SCN)$_2$Ni(NCS)(APH)] (a dimer containing six-coordinate Ni(II) requires the presence of four thiocyanato bridges which has not ever been observed and will not be considered) can be ruled out with certainty. The two remaining reasonable general structural possibilities are as follows: (c) an infinite zigzag-type polymer structure. The first possibility within c is the zigzag chain *cis*-thiocyanate-N, *cis*-thiocyanate-S (Scheme 1), proposed [47] for M(bpy)(NCS)$_2$ (M = Mn, Fe, Co and bpy = 2,2-bipyridine). There are two other zigzag-type structural possibilities that can be proposed based on our data (Scheme 2).

With the assumption that the nitrogens from APH lie in the equatorial plane of the metal octahedra with the requirements that the N atoms from APH are *cis* to each other and the N and S atoms from different thiocyanate groups that bridge the same metal atoms also lie *cis* to each other, the differences between the zigzag chains shown are the result of differences in the coordination position of the S atoms of bridging thiocyanato groups that bond to different metal atoms. In *trans*-thiocyanate-N, *cis*-thiocyanate-S, the S atoms lie in the plane of the octahedra, while in *cis*-thiocyanate-N, *trans*-thiocyanate-S they are located in the *trans* positions above and below the equatorial plane of the octahedra; the symmetry of the local coordination environment for both formulae is C_{2v}; and (d) an infinite helical polymer chain containing six-coordinate Ni(II) centres similar to that found for Ni(tam)$_2$(NCS)$_2$ (tam = thioacetamide) [47] which has the same bridging groups as the above linear chain polymers, but they are arranged in a near-orthogonal orientation forming a helical chain along the 3_1 screw axis. If Ni(APH)(NCS)$_2$ does have a type of helical chain similar to that of Ni(tam)$_2$(NCS)$_2$, one APH molecule can be thought of as replacing the two thioacetamide ligands giving a local coordination environment similar to that of the second zigzag-type structure. The present results do not allow for further refinement of our choice between (c) and (d).

Finally, it is clear from the foregoing work that the thermal decomposition of monomeric Ni(II)/APH complexes results in condensation to polymeric species. This is fully consistent with metal centres avoiding coordinative unsaturation through anion bridging in the absence of steric hindrance from the organic ligand.

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