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STUDIES ON COORDINATION COMPOUNDS—VIII. SYNTHESES, STRUCTURAL, MAGNETIC, SPECTRAL AND THERMAL PROPERTIES OF SOME COBALT(II), NICKEL(II) AND COPPER(II) COMPLEXES OF 2-AMINOPYRIMIDINE*

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Abstract—The complexes bis[triaqua(2-aminopyrimidine)-μ-sulphato-O,O′-cobalt(II)] dihydrate (**1**), *catena*-[diaqua(2(2-aminopyrimidine))-μ-sulphato-O,O′nickel(II)]2-aminopyrimidine (**2**), [pentaaqua(2-aminopyrimidine)nickel(II)] sulphate 2-aminopyrimidine (**3**) and *catena*-[aqua(2(2-aminopyrimidine))-μ-sulphato-O,O′-copper(II)] dihydrate (**4**) were prepared, structure determined by X-ray methods and physical properties studied by magnetic, IR, NMR, EPR and reflectance methods. The thermal behaviour was studied by TG and mass spectrometric methods. The results are discussed on a structural basis.

The physiological importance of pyrimidine and its derivatives, eg. 2-aminopyrimidine, has led to great interest in their complexation tendency with metal ions, especially with transition metal ions.[1]

The IR spectrum of 2-aminopyrimidine or its metal complexes has been treated in several papers.[2] In the same connection the magnetic,[2a–2c,2h] reflectance spectral[2a–2c,2h] data and thermal behaviour[2h] were also considered.

The crystal structure of 2-aminopyrimidine[3] and its several mixed metal complexes[4] has been determined, but not used as a basis of discussion of the correlation between the above mentioned physical properties and structure of the complexes. However, attempts in this direction were done recently in two short papers[5,6] and are continued more thoroughly in this paper.

EXPERIMENTAL

Reagents, syntheses and analyses¶

Synthesis of Co(2-AP)$SO_4 \cdot 4H_2O$ (**1**). For preparation of the complex 28.11 g (0.1 mol) $CoSO_4 \cdot 7H_2O$ (*Baker Analyzed Reagent*, Noury-Baker) and 9.51 g (0.1 mol) 2-aminopyrimidine (*Purum*, Fluka AG) were dissolved in 100 cm^3 of water. The solution was allowed to stay in open glass at room temperature. After 2 weeks pale red crystals separated. The crystals were filtered (after 2 months), washed with methanol, dried and stored in a desiccator. Cobalt was determined as Co_3O_4 by combustion at 900° in an electric oven (Thermolyne

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¶ 2-AP = 2-aminopyrimidine = $C_4H_5N_3$.

1400), sulphate gravimetrically as $BaSO_4$ and other elements by microcombustion analyses. Found: C, 14.6; H, 4.1; N, 13.0; S, 9.9; Co, 18.3. Calc. for $Co(C_4H_5N_3)SO_4 \cdot 4H_2O$ (m.w. 322.16): C, 14.9; H, 4.1; N, 13.0; S, 9.9; Co, 18.2%.

Synthesis of $Ni(2\text{-}AP)_3SO_4 \cdot 2H_2O$ (**2**). $NiSO_4 \cdot 6H_2O$ [26.29 g (0.1 mol), *p.a.*, Merck] and 9.51 g (0.1 mol) 2-AP were dissolved in water. The solution was allowed to stand at room temperature, filtered after 1 day, the clear solution evaporated to 70 cm^3 (Rotavapor-R, Büchi). After several days small green crystals separated, were filtered, washed with methanol, dried and stored in a desiccator. Nickel was determined gravimetrically as dimethylglyoximate from ammoniacal solution, the other elements as above. Found: C, 29.2; H, 4.1; N, 26.1. Calc. for $Ni(C_4H_5N_3)_3SO_4 \cdot 2H_2O$ (m.w. 476.11): C, 30.3; H, 4.0; N, 26.5%.

Synthesis of $Ni(2\text{-}AP)_2SO_4 \cdot 5H_2O$ (**3**). From the mother liquor above a pale green fine-grained precipitate separated within 1 week, which was handled as above and was established to be a transition form between the complexes **2** and **3**.

The obtained filtrate was allowed to evaporate further in an open decanter glass. Within 2–3 weeks long, pink green crystals (complex **3**) were separated and handled as above. This complex was obtained more rapidly leaving the above intervening phase. The analyses were performed as for complex **2**. Found: C, 21.3; H, 4.8; N, 19.1; S, 7.3; Ni, 13.5. Calc. for $Ni(C_4H_5N_3)_2SO_4 \cdot 5H_2O$ (m.w. 435.05): C, 22.1; H, 4.6; N, 19.3; S, 7.4; Ni, 13.5%.

Synthesis of $Cu(2\text{-}AP)_2SO_4 \cdot 3H_2O$ (**4**). This complex was prepared by dissolving separately 2.50 g (0.01 mol) $CuSO_4 \cdot 5H_2O$ (*p.a.*, Merck) and 5.718 g (0.06 mol) 2-AP into small amounts of water, mixed and diluted to 100 cm^3, made 0.07 M with respect to sulphuric acid. After 2–3 days small green crystals were separated, filtered, washed with water, dried at room temperature and stored in a desiccator. Yield 2.2 g (54.5% from theory). Copper was determined electroanalytically from acid solution and other elements as above. Found: C, 23.3; H, 4.0; N, 20.6; S, 7.9; Cu, 15.9. Calc. for $Cu(C_4H_5N_3)_2SO_4 \cdot 3H_2O$ (m.w. 403.86): C, 23.8; H, 4.0; N, 20.8; S, 7.9; Cu, 15.7%.

Physical measurements

For magnetic susceptibility measurements a home constructed variable-temperature Gouy equipment described in the literature[7] was used. The balance was a Mettler M 5 micro-balance, the measurement chamber in the Dewar vessel from copper, the sample tube from Teflon and the temperature regulators of Honeywell type. The calibration compound was $HgCo(SCN)_4$.[8] Measurements were performed in nitrogen (40 cm^3 min^{-1}) at 80.2–331.1 K with 20° intervals generally and in each temperature range at least five different magnetic field strengths.

The dependence of the susceptibilities on the absolute temperature was linear and followed the Curie–Weiss law:

$$\chi'_M = C/(T+\Theta) \qquad (1)$$

where χ'_M is the molar susceptibility of the complex corrected for diamagnetism using Pascal's constants,[9] C the Curie constant, Θ the Weiss constant and T the absolute temperature. The χ'_M values were fitted by the method of least squares to equation (1) and the values of the constants C and Θ evaluated. The effective magnetic moments μ_{eff} in Bohr magnetons were calculated from the χ'_M values by the known method.[9]

The EPR spectra of the complexes were recorded for powders of about 3 cm high beds in quartz tubes on Varian E-6 and E-12 spectrometers. The pyrene anion ($g = 2.00266$)[10] and 2,2-diphenyl-1-picrylhydrazyl (DPPH), ($g_{DPPH} = 2.0036$)[11] were used in another quartz tube in the dual cavity as reference compounds. Spectra were run generally at room temperature (295 ± 2 K), because variations of temperature between 113 and 298 K hardly affected the spectrum. The running time was 8 min, the scan range 1000 G, the field set 3100 G, the modulation amplitude 0.032 G, the modulation frequency 100 kHz, the time constant 0.3 and the microwave frequency 9.271 GHz. With the g value of the reference, the magnetic field was determined accurately, because the field is not exact. The correction was of the order 20 G, with which the field strengths corresponding to the $g_\parallel$ and $g_\perp$ values were corrected, after which the exact g values were obtained.

The reflectance spectra of the complexes were run from powdered compounds in paraffin (*Uvasol*, E. Merck) pastes spread on a filter paper on a Beckman DK-2A spectrophotometer in the wavelength range 360–1000 nm. A filter paper treated with paraffin was used as a reference.

The ^1H NMR spectra of 2-AP and the complexes were taken in 1.0–11 wt% solutions in $(CD_3)_2SO$ and D_2O (*Uvasol*, 99 and 99.75% for spectroscopy, E. Merck) with a Perkin–Elmer R 12 B NMR spectrometer equipped with a double resonance accessory for radiation at 306.7 K. The results showed no signals due to complexes, except for complex **1** in D_2O with two flattened and broad singlets at 7.3 and 10.6 ppm from the internal standard NaTPS (the sodium salt of 3-trimethylsilylpropanesulphonic acid, $C_6H_{15}NaO_3SSi$, *Uvasol*, E. Merck), when the sample concentration was 4.11%. The signal of D_2O was broadened and transformed to lower field, $\delta(D_2O) = 5.8$ ppm. Standard concentration was 2–5 mg cm^{-3} of solvent. The non-appearance of signals arising from the complexes is obviously due to the presence of the paramagnetic metal ions, which may cause a broadening of the signals so that they cannot be observed.[12]

The mass spectra of the complexes taken via the solid inlet from solid samples in glass capillary sealed on the other end with excitation energies 16–70 eV showed no molecular peaks of the complexes, but only the mass spectrum of 2-AP or of some polymer products. The mass spectrometer was a Perkin–Elmer 270 B mass spectrometer.[13]

The infrared spectra of 2-AP, metal sulphates and the complexes were obtained in KBr disks [1.4–2 mg per 200 mg of KBr (*Uvasol*, E. Merck)] on a Perkin–Elmer 457 grating infrared spectrophotometer[14] in the wavelength range 4000–250 cm^{-1}. The reference was an equally thick KBr disk.

Thermogravimetric analyses of the complexes were done in a static air atmosphere. The apparatus was a Fisher 100 TGA system[14] equipped with the Linear Temperature Programmer Model 360, a Cahn derivative box, RG Electrobalance and a three-pen recorder of model Multicorder MC 611-SH (Watanabe Instruments Co.). A self-built amplifier was used with the recorder for the input of the DTG signals. The heating rate for TG was 5 C min^{-1} and sample weights: (**1**) 9.76, (**2**) 9.54, (**3**) 9.81 and (**4**) 9.48 mg.

Thermal ellipsoids in the ORTEP views in Figs 1–4 are drawn at 50% probability level for the non-hydrogen atoms.[15]

RESULTS AND DISCUSSION

Description of the structures

Structure of $[Co(2\text{-}AP)(H_2O)_3SO_4]_2 \cdot 2H_2O$ (**1**). This complex is a dimer as seen in Fig. 1. The structure shows a distorted octahedral coordination around the cobalt(II) atoms. Two sulphate ions form bridges between the two metal atoms being coordinated through two oxygen atoms to different metal atoms. Thus there is double sulphate bridge between the metal centres. Three from four water molecules are coordinated to each metal ion and the fourth is uncoordinated in the crystal lattice. Further, one 2-AP molecule is coordinated through the ring nitrogen N(1) to each Cobalt(II) atom.[15]

Structure of $[Ni(2\text{-}AP)_2(H_2O)_2SO_4](2\text{-}AP)$ (**2**). Figure 2 shows the main unit of the complex **2**. In the structure one sulphate ion forms through its two oxygen atoms a bridge between two nuclei leading to a chain structure in the *a*-direction. The coordination sphere around the metal atom is again a distorted octahedral being coursed through two ring nitrogen [N(1) and N(4)] coordinated 2-AP molecules, two water molecules and two oxygen atoms of different sulphate ions. One uncoordinated 2-AP molecule forms columns between the chains.[15]

Structure of $[Ni(2\text{-}AP)(H_2O)_5]SO_4(2\text{-}AP)$ (**3**). The structure of the complex **3** is ionic (Fig. 3). The coordination sphere around the nickel(II) atom is a six-coordinated, distorted octahedral, five water molecules and one N(1) coordinated 2-AP molecule forming the coordination sphere. The sulphate anion and the other 2-AP molecule are uncoordinated in the crystal lattice.[15]

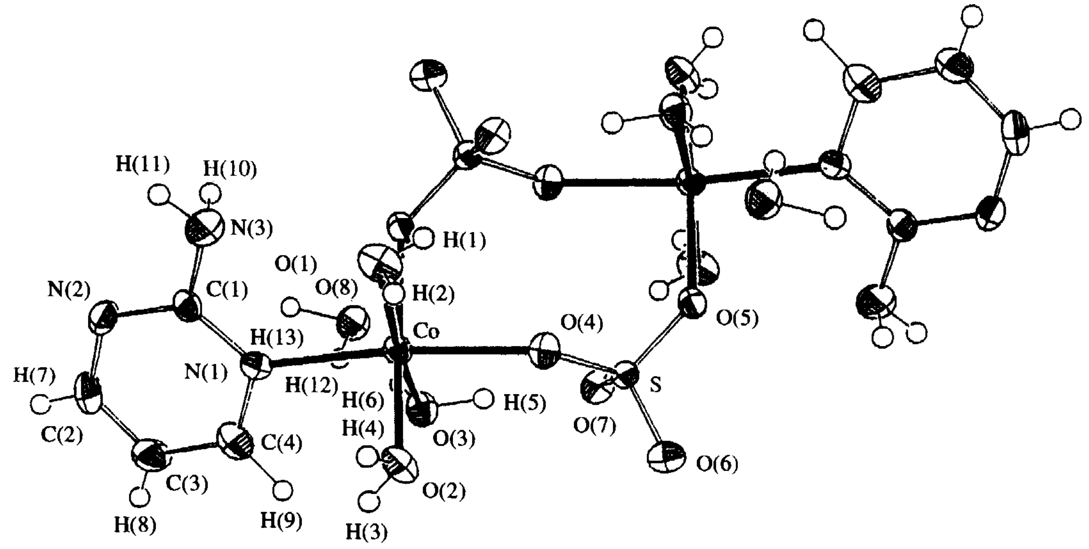

Fig. 1. ORTEP view of $[Co(2\text{-}AP)(H_2O)_3SO_4] \cdot 2H_2O$ (**1**).

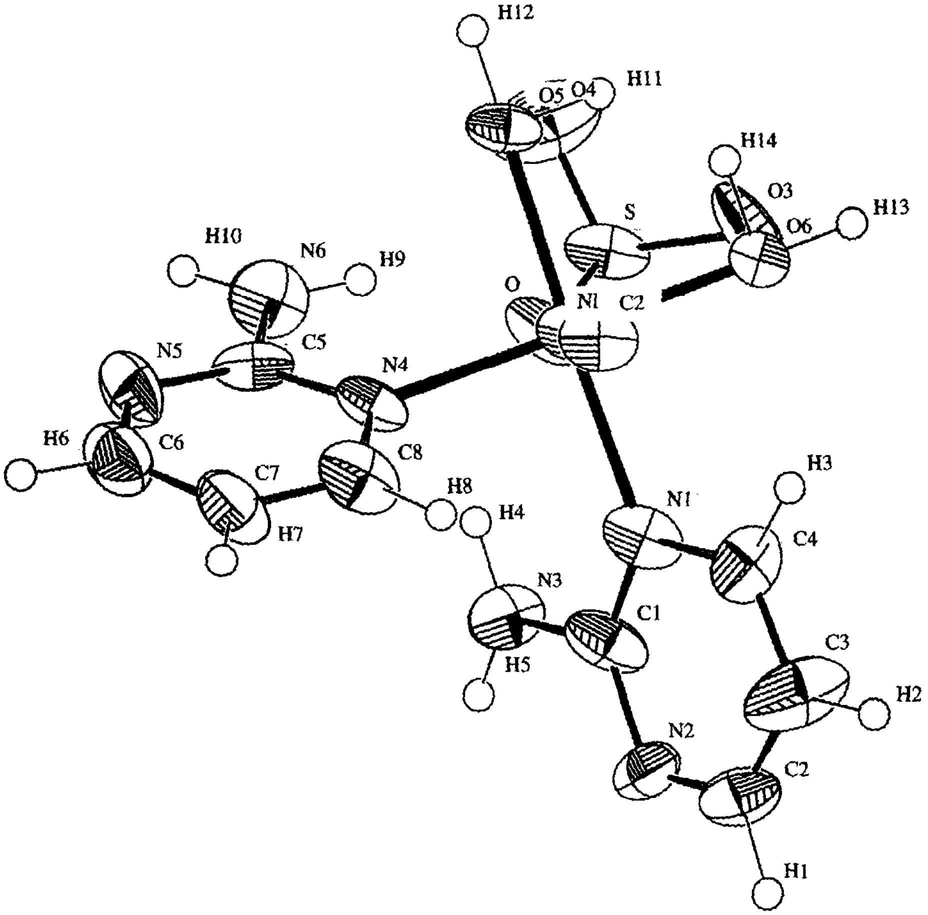

Fig. 2. ORTEP view of unit [Ni(2-AP)$_2$(H$_2$O)$_2$SO$_4$] of the complex (**2**).

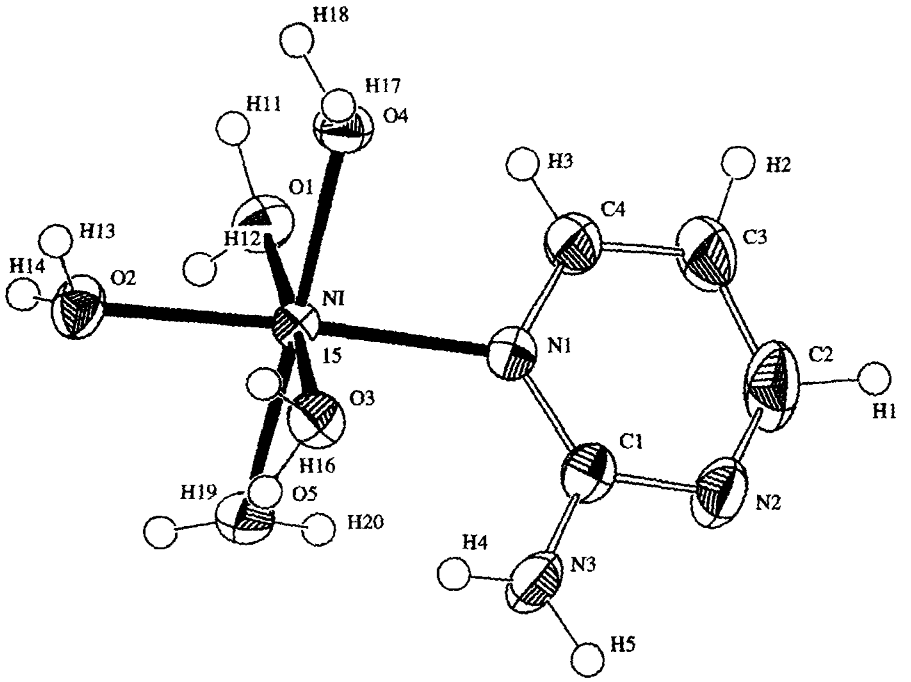

Fig. 3. ORTEP view of the cation [Ni(2-AP)(H$_2$O)$_5$]$^{2+}$ of the complex (**3**).

Structure of $[Cu(2\text{-}AP)_2(H_2O)SO_4]\cdot 2H_2O$ (**4**). The ORTEP view of the complex **4** is shown in Fig. 4. The coordination sphere around the copper(II) ion is a square pyramid. The five coordination is coursed through two N(1) coordinated 2-AP molecules, one water molecule [O(4) coordinated], one O(1) atom of one sulphate ion and one O(3) atom of the other sulphate ion in the apical position. There are a further two uncoordinated water molecules in the crystal lattice. The sulphate anions effect a chain structure between the copper(II) cations in the *a*-direction.[15]

Table 1. Metal coordination distances (Å)

Complex	M—O	M—N[a]
1	2.075(5)–2.169(5)	2.201(6)
2	2.051(9)–2.102(8)	2.13(1)
3	2.045(3)–2.096(3)	2.116(3)
4	1.937(4)–2.339(4)	2.045(5)

[a] M = Co, Ni or Cu.

The metal coordination sphere. The metal coordination distances vary generally little as seen in Table 1. Metal—2-1AP distances vary between 2.045(5) [Cu—N(1)] and 2.201(6) [Co—N(1)], metal—O(H_2O) distances from 1.937(4) [Cu—O(4)] to 2.119(5) [Co—O(1)] and metal—O(SO_4) distances from 1.948(4) [Cu—O(1)] to 2.339(4) [Cu—O(3)] Å. The exceptional last mentioned limit value is the sulphate oxygen O(3) atom distance at the apical position to the copper atom.[15]

On the basis of the coordination distances it is not possible to conclude directly on the penetration ability of the water, sulphate or 2-AP molecules with respect to the metal atom and to correlate it with the ionic, dimeric or chain structure of the complexes. However, in most cases the metal–oxygen distances are shortest for water molecules as expected on the basis of its size.

Hydrogen bond systems. In all four complexes **1**–**4** there is a considerable hydrogen bond network stabilizing the crystal structure. The hydrogen bonds are of three to five different types. In the complex **1** there are water–sulphate oxygen–hydrogen bonds within the same asymmetric unit, also

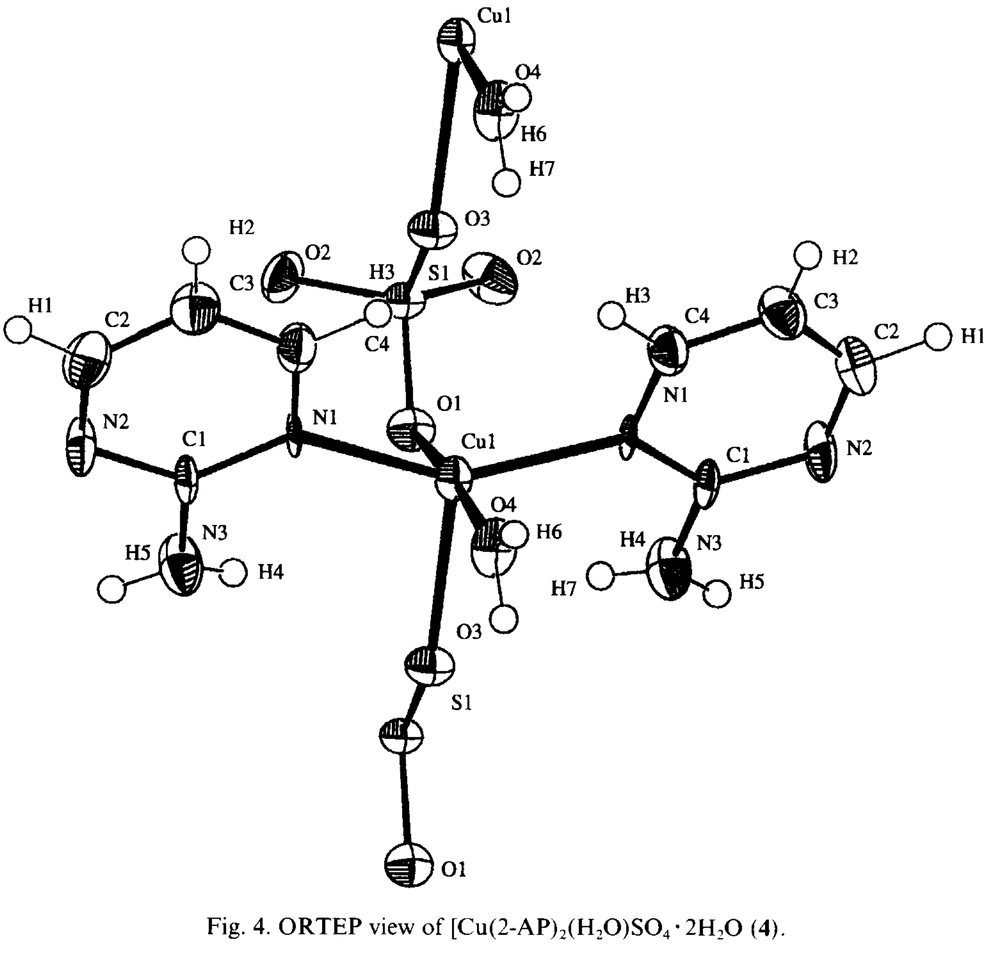

Fig. 4. ORTEP view of $[Cu(2\text{-}AP)_2(H_2O)SO_4\cdot 2H_2O$ (**4**).

between neighbouring asymmetric units and water–pyrimidine ring nitrogen–hydrogen bonds between different asymmetric units.[15]

In the complex **2** there are within the same asymmetric unit amino-nitrogen– and ring carbon–sulphate oxygen and water–pyrimidine ring nitrogen–hydrogen bonds and between neighbouring asymmetric unit amino-nitrogen–pyrimidine ring nitrogen and water–sulphate oxygen–hydrogen bonds.[15]

In the complex **3** there are between different asymmetric units hydrogen bonds from amino-nitrogen to sulphate oxygen and to pyrimidine ring nitrogen atoms and water–sulphate oxygen and pyrimidine ring nitrogen–hydrogen bonds.[15]

In the complex **4** the situation is the same as in the complex **3**, except that there is a water–sulphate oxygen–hydrogen bond within the asymmetric unit, but not a water–pyrimidine ring nitrogen–hydrogen bond between different asymmetric units.[15]

Magnetic behaviour, EPR and reflectance spectra

The diamagnetic corrections were calculated from Pascal's constants to be the following: (**1**) -1.545×10^{-4}, (**3**) -2.178×10^{-4}, (**4**) -1.908×10^{-4} $cm^3\ mol^{-1}$. With these corrected values of the molar magnetic susceptibilities χ'_M and from them calculated values of the effective magnetic moments μ_{eff} (B.M.) are given in Table 2. When fitting the χ'_M values by the method of least-squares to the equation (1) the following values of the constants C and Θ were obtained: (**1**) 3.353, 26.0, (**3**) 1.311, 9.9, (**4**) 0.544, 26.4, respectively. The dependence of the χ'_M and μ_{eff} values on the temperature is smooth and increases in the order Cu < Ni < Co in the temperature range 80–330 K.

Generally the orbital contribution to the value of μ_{eff} is higher the greater the dependence of μ_{eff} on the temperature. Therefore the orbital contribution in the present case should increase on the basis of the C values in the order Cu < Ni < Co, in which order the C values increase. On the other hand the present systems are magnetically dilute and therefore the intramolecular antiferromagnetism should lead to positive values of Θ and it would increase in the order Ni < Co < Cu. However, the iterations for the dimer and chain structures based on the van Vleck's equations[9] did not converge pointing to the absence or very low level of the antiferromagnetic effect.

From the EPR spectra at 298 ± 2 K the following g values were derived: (**1**) 2.004 (g), (**3**) 2.003 (g), (**4**) 2.104(1) ($g_\perp$), 2.32(1) ($g_\parallel$), 2.18(1) (g). In octahedral cobalt(II) and nickel(II) complexes the strong field d^7 and d^8 configurations are $(t_{2g})^5(e_g)^2$ and $(t_{2g})^6(e_g)^2$, respectively, and the presence of low-lying excited states results in large zero-field splitting. As a result only one transition is observed and the g value is highly isotropic as the obtained results above show.[16]

For the copper(II) complex (**4**) the obtained g-values correspond to literature values presented for octahedral copper(II) complexes.[17,18] Therefore, the change from octahedral to square pyramidal coordination would not considerably affect the g values.

On the basis of the C values from the magnetic susceptibility measurements from the equation (2):

Table 2. Molar magnetic susceptibilities χ'_M (e.m.u.) and effective magnetic moments μ_{eff} $[=2.828(\chi'_M T)^{1/2}]$ (B.M.) at various temperatures (K)

Complex	**1**		**3**			**4**	
T (K)	$\chi'_M \times 10^3$	μ_{eff}	$\chi'_M \times 10^3$	μ_{eff}	T (K)	$\chi'_M \times 10^3$	μ_{eff}
—	—	—	—	—	333.1	1.486	1.990
—	—	—	—	—	323.1	1.566	2.011
298.2	10.35	4.968	4.205	3.167	303.2	1.680	2.018
278.2	10.97	4.941	4.514	3.169	282.2	1.787	2.008
258.2	11.79	4.933	4.944	3.195	263.3	1.886	1.993
238.2	12.64	4.907	5.312	3.181	242.9	2.000	1.971
218.2	13.77	4.902	5.814	3.185	222.9	2.174	1.969
198.2	14.95	4.868	6.335	3.169	203.1	2.367	1.961
178.2	16.47	4.844	6.988	3.156	183.4	2.546	1.932
158.2	18.21	4.799	7.771	3.135	163.2	2.822	1.919
138.2	20.81	4.796	8.905	3.137	143.2	3.227	1.922
118.2	23.58	4.721	10.38	3.132	123.2	3.645	1.895
103.2	25.47	4.585	11.30	3.054	102.1	4.348	1.884
90.2	—	—	12.90	3.050	—	—	—
80.2	30.95	4.455	—	—	—	—	—

$$g = 2.828\{C/[S(S+1)]\}^{1/2}. \qquad (2)$$

Calculated "spin-only" values are for the complexes: (**1**) 2.674, (**3**) 2.29, (**4**) 2.41. Compared with g values obtained from the EPR spectra this would mean that the orbital contribution should increase in the present case in the order Cu < Ni < Co, in agreement with the conclusion above. On the other hand the metal–metal interaction would increase in the order Ni < Co < Cu, in which order the metal–metal distance decreases: (**3**) 7.241(1), (**2**) 6.207(4), (**1**) 5.233(2), (**4**) 4.927(2) Å. This is in agreement with the ionic and dimeric or chain structural properties of the complexes.

The electron delocalization cannot be estimated for the cobalt and nickel complex on the basis of the g values obtained from the EPR spectra, but the magnetic results show that there must be comparatively little electron delocalization ($\leqslant 5\%$). The same conclusion is obtained for the copper complex on both bases. Further, the anisotropy in g indicates the presence of a fairly large component of low symmetry in the ligand field in agreement with the coordination sphere in the copper(II) complex (**4**).

The absorption maxima of the reflectance spectra of the studied complexes with their assignments[19] are presented in Table 3. The cobalt complex showed an absorption maximum at 486 nm, which corresponds to the electron transition $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and two weak shoulders at 448 and 625 nm.

Both nickel complexes studied showed strongest absorption near 650 nm, which probably corresponds to the transition $^3A_{2g}(F) \rightarrow {}^1E_g(D)$ in octahedral nickel(II) complexes.[20] At 700–720 nm the spectra showed a very weak shoulder, which usually is not met in octahedral nickel(II) complexes, and which is assumed to be due to a large tetragonal disturbance in the complex.[21,22] In the spectrum of the complex **3** this shoulder was almost unobserved. These results are in agreement with the octahedral coordination in the present cobalt(II) and nickel(II) complexes.[20,23]

On the basis of the reflectance spectrum of the copper(II) complex (**4**) the coordination number of the copper atom would be six and the complex structure octahedral, O_h symmetry. The O_h symmetry is, however, disturbed due to low symmetry in ligand field components and the structure is in reality a pentacoordinated square pyramid around the copper atom and not octahedral.

Infrared spectra

In Table 4 the most important strong or medium bands of the spectra of the complexes are presented and are tentatively assigned by comparing the complex spectra with the spectra of the ligand 2-aminopyrimidine and the metal sulphates. The coordination to the metal causes shifts of the bands of the ligands to lower or higher frequencies with different intensities. The shift direction depends on the structure of the complex, the nature of the normal vibration and the effect of coordination on it.[24]

The vibration spectra of metal complexes are divided into the high frequency, 4000–650 cm^{-1} and low or far frequency, 650–50 cm^{-1}, area. Vibrations of the ligands appear in the high frequency area, whereas vibrations due to the metal–ligand coordination bonds are in the low area.[25,26]

The interpretation of the IR spectra of the complexes and of the shifts of the absorption maxima is specially rendered difficult, because essential vibrations appear within the same wavelength ranges. The O—H and N—H stretching vibrations appear in the spectra of the complexes in the range

Table 3. Reflectance spectral data for the 2-aminopyrimidine complexes

	Absorption		Assignment
Complex	λ (nm)	ν (cm^{-1})	(Transition)
$[Co(2\text{-}AP)(H_2O)_3SO_4]_2 \cdot 2H_2O$	448 (sh)[a]	22320	—
	486	20580	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
	625 (sh)	16000	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$
$[Ni(2\text{-}AP)_2(H_2O)_2SO_4](2\text{-}AP)$	655	15270	$^3A_{2g}(F) \rightarrow {}^1E_g(D)$
	720 (sh)	13890	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$
$[Ni(2\text{-}AP)(H_2O)_5]SO_4(2\text{-}AP)$	642	15580	$^3A_{2g}(F) \rightarrow {}^1E_g(D)$
	700 (sh)	14290	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$
	1075	9300	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$
$[Cu(2\text{-}AP)_2(H_2O)SO_4] \cdot 2H_2O$	398 (sh)	25310	Spin forbidden
	710	14090	$^2E_g(D) \rightarrow {}^2T_{2g}(D)$

[a] sh = shoulder.

Table 4. Selected (strong or medium) infrared bands cm^{-1} of the complexes **1**–**4**[a]

1	**2**	**3**	**4**	Assignment
3500	3400	3460	3480	ν(OH), H_2O coord.
3370	3320	3360	3400	ν_{as}(NH)
3120	3180	3200	3135	ν_s(NH)
1640	1650	1655	1642	$\delta(NH_2)$, $\delta(H_2O)$
1590	1595	1590	1590	$\delta(H_2O)$
1578	1575	1575	—	ν(C=C), ν(C=N), ring ν.
—	1560	1565	1567	ν(C=C), ν(C=N), ring ν.
1495	1490	1500	1492	ν(C=C), ν(C=N), ring ν.
—	1373	1370	—	$\nu(C_{aryl}$—N)
1367	1363	1360	1362	$\nu(C_{aryl}$—N)
1200	1180	1225	1198	δ (CH), δ (NH) in plane
—	1150	—	1140	$\nu_{3a}(SO_4)$
1100	1130	1100	1115	$\nu_{3a}(SO_4)$, $\nu_3(SO_4)$
—	1070	—	1085	$\nu_{3b}(SO_4)$
1010	1050	—	1030	$\nu_{3b}(SO_4)$
983	980	980	970	$\nu_1(SO_4)$
800	805	795	787	δ(NH) out of plane
—	790	770	—	δ(CH), $\delta(H_2O)$ coord.
660	660	660	—	$\delta(H_2O)$
615	640	615	620	$\delta_4(SO_4)$
—	610	—	600	$\delta_4(SO_4)$
530	527	520	520	ν(M—N)
460	475	460	477	ν(M—N)
425	425	—	440	ν(M—O), SO_4 bidentate
400	—	400	410	ν(M—O), H_2O

[a] ν = stretching, δ = bending, as = antisymmetric, s = symmetric.

3500–3100 cm^{-1}, the absorption of non-bonded water being especially strong and broad and covering other absorptions in the same area. Likely H—O—H and H—N—H bending vibrations of water and 2-aminopyrimidine, respectively, appear in the same area[27] at 1660–1640 cm^{-1} and C=C and C=N vibrations fall together with the ring vibrations of pyrimidine in the ranges 1580–1560 and 1500–1480 cm^{-1}.[27,28] Vibrations of the coordinated water molecules are also observed at 1590, 790–770 and 660 cm^{-1}.[29,30] The complexes **2** and **3** contain only coordinated water molecules.

Similarly the C_{aryl}—N vibration band in the spectrum of 2-AP is shifted as undivided or divided into two bands as in the complex spectra of the nickel complexes, which contain both uncoordinated and coordinated 2-AP molecules.

The complex spectra show the sulphate stretching and bending bands at 1150–1100, 1085–1010, 990–970 and 640–615 cm^{-1}.[31] The bands at 530–460 and 425–400 cm^{-1} are probably due to M—N and M—O stretching vibrations, respectively.[32,33]

The results in Table 4 show that the C_{aryl}—N stretching bands at 1360–1367 and 1370–1373 cm^{-1} would indicate coordinated and uncoordinated 2-AP molecules, respectively. The coordinating atom of 2-AP and coordination or non-coordination of water, however, cannot be concluded from the spectra. This requires the crystal structure determination.[15] This conclusion casts doubt on the interpretations in some of the papers referred to above.

Further, the numbers 4, 5, 8 and 8 of the SO_4 stretching and bending bands in the spectra of the complexes **3**, **1**, **4** and **2**, respectively, point to a non-coordinated and bidentately coordinated sulphate ion in order of lowering symmetry from T_d and increasing disturbance of the other coordinated ligands, H_2O and 2-AP.[15,34] The O—S—O bending vibrations at 650–450 cm^{-1} and the metal–ligand vibrations[34] at 900–400 cm^{-1} disturb each other. The assignment of the band positions without normal coordinate analysis is to some extent uncertain.

Thermal properties and mass spectra

The molecular peak of any of the four complexes was not obtained even though the conditions of the mass spectral measurements were varied. Typical for mass spectra of all complexes was that they were mainly mass spectra of 2-aminopyrimidine. The strongest peaks in the mass spectra were the molecular peak ($m/z = 95$) of 2-aminopyrimidine and its cleavage products. Most typical was the peak $m/z = 68$ corresponding to the cleavage of HCN as by aromatic amides.[35] This cleavage obviously happens during thermal decomposition. Also the peak $m/z = 18$ corresponding to the cleavage of water was strong in the spectra. It implies the easy cleavage of water from the complexes, especially from the cobalt complex.

By using low ionization energy and the highest possible sensitivity also weak peaks above $m/z = 95$ were observed in the spectra. For all complexes the groups $m/z = 119$, 120, 121 were observed in the spectrum. Generally, the higher ionization energy used the stronger was the cleavage tendency of the ligand.

The analysis of the TG curve of the cobalt complex **1** is shown in Table 5. The decomposition of the complex begins at about 60°C by the loss of three water molecules. This was followed by retarded decomposition of the complex from 200 to 380°C, which is responsible for the loss of one [the O(3) coordinated] water and HCN molecule corresponding to aromatic amides in the mass spectrometer typical cleavage reaction of HCN.[35] In the next phase the organic residue escaped at 380–665°C. The $CoSO_4$ formed is stable from 665–

Table 5. TG data for the 2-AP complexes **1**–**4**

Process	Temperature range (°C)	Residue (% from total)	
		Found	Calc.
$[Co(C_4H_5N_3)(H_2O)_3SO_4]\cdot H_2O$			
$\downarrow -3H_2O$	60–200		
$[Co(C_4H_5N_3)(H_2O)SO_4]$		84.0	83.2
$\downarrow -H_2O-HCN$	200–380		
$Co(C_3H_4N_2)SO_4$		69.8	69.2
$\downarrow -C_2H_2-H_2NCN$	380–665		
$CoSO_4$	665–785	40.7	43.1
$\downarrow -SO_3$	785–985		
Co_3O_4	985→	24.8	24.9
$[Ni(C_4H_5N_3)_2(H_2O)_2SO_4](C_4H_5N_3)$			
$\downarrow -C_4H_5N_3$	150–220		
$[Ni(C_4H_5N_3)_2(H_2O)_2SO_4]$		77.6	80.0
$\downarrow -2H_2O$	220–330		
$Ni(C_4H_5N_3)_2SO_4$		70.5	72.4
$\downarrow -C_4H_5N_3-HCN$	330–390		
$Ni(C_3H_4N_2)SO_4$		45.3	46.7
$\downarrow -C_2H_2-H_2NCN$	390–760		
$NiSO_4$		29.6	32.5
$\downarrow -SO_3$	760–920		
NiO	920→	13.8	15.7
$[Ni(C_4H_5N_3)(H_2O)_5]SO_4(C_4H_5N_3)$			
$\downarrow -4H_2O$	110–160		
$[Ni(C_4H_5N_3)(H_2O)]SO_4(C_4H_5N_3)$		83.1	83.4
$\downarrow -H_2O$	160–185		
$[Ni(C_4H_5N_3)]SO_4(C_4H_5N_3)$		79.8	79.3
$\downarrow -2HCN$	185–325		
$[Ni(C_3H_4N_2)_2]SO_4$		66.1	66.9
$\downarrow -2(C_2H_2+H_2NCN)$	325–650		
$NiSO_4$		35.9	35.6
$\downarrow -SO_3$	650–950		
NiO	950→	17.1	17.2
$[Cu(C_4H_5N_3)_2(H_2O)SO_4]\cdot 2H_2O$			
$\downarrow -3H_2O$	90–170		
$Cu(C_4H_5N_3)_2SO_4$		84.4	86.6
$\downarrow -2HCN$	170–210		
$Cu(C_3H_4N_2)_2SO_4$		70.9	73.2
$\downarrow -2(C_2H_2+H_2NCN)-\frac{1}{2}SO_3$	210–550		
$CuO\cdot(SO_3)_{0.5}$		27.4	29.6
$\downarrow -\frac{1}{2}SO_3$	550–840		
CuO	840→	18.1	19.7

785°C. The end product was Co_3O_4 above 985°C, the amount being 24.8% from the TG curve compared with 24.9% calculated.

The nickel(II) complex (**2**) is stable to 150°C, then losing one (the non-coordinated) 2-AP molecule to 220°C. Next two water molecules were lost slowly between 220 and 330°C. Thirdly, a more rapid loss of one [the N(1) coordinated] 2-AP and one HCN molecule occurred. The rest decomposed slowly to $NiSO_4$, reaching at 760°C. This decomposed to NiO between 760 and 920°C. The yield of NiO was 13.8, calculated as 15.7%.

In the case of the nickel(II) complex (**3**), the loss of the first four water molecules began at 110°C followed by slow decomposition of the rest. First the last water molecule [the O(4) coordinated] was removed followed by two HCN molecules. At 650°C $NiSO_4$ remained and was decomposed between 650 and 950°C to NiO. The yield of NiO was 17.1 and calculated as 17.2%.

In the TG curve of the copper(II) complex (**4**), at first three water molecules were lost at 90–170°C. In the second phase two HCN molecules were eliminated at 170–210°C. In the third phase the organic residue and SO_3 were lost between 210 and 550°C, and $2CuO \cdot SO_3$ was left. SO_3 was further lost from 550 to 840°C leaving CuO as the end product (found 18.1, calculated 19.7%).

CONCLUSIONS

All complexes were crystallized from aqueous solutions. The copper(II) complex (**4**) was formed most easily, in about 2–3 days from dilute sulphuric acid solution. The separation of cobalt(II) and nickel(II) complexes took a long time, several months. They were crystallized from concentrated solutions.

Three kinds of nickel(II) complexes were separated. The triclinic nickel(II) complex (**2**) crystallized in a small amount in the beginning of the crystallization. After this a powder-like complex separated and at the end the orthorhombic complex (**3**). This is obviously the end product in the synthesis, and if the first and second product were not separated the end product was the orthorhombic form only. The second phase product is a mixture of the first and last product without exact composition, but nearest to the last.

A part of the complexes is a distorted octahedral with metal coordination number 6: the cobalt(II) complex (**1**), a dimer; the nickel(II) complex (**2**), a chain; the nickel(II) complex (**3**), a monomer, ionic. The copper(II) complex (**4**) is a pentacoordinated, square pyramid, chain structure.

The coordination of 2-aminopyrimidine happens in every complex through one ring nitrogen only to the central metal atom. In the nickel(II) complex (**3**) only the sulphate ion is not bonded to a metal atom.

On the basis of the values of the magnetic moments and EPR and reflectance spectral data all studied complexes are distorted octahedral coordinated complexes with coordination number 6, except copper(II) complex, which has square pyramidal coordinated nucleus with coordination number 5 as the X-ray structure analysis shows.

On the basis of the IR spectra without normal coordinate analysis it is not possible to conclude that the coordination of 2-aminopyrimidine ligand would happen only through one ring nitrogen to the central metal atom, if the crystal structure is not known. Similarly the coordination or non-coordination of water molecules cannot be concluded, but that of the sulphate ion can, on the basis of the comparative IR spectral analysis.

The thermal decomposition of the nickel(II) complex (**2**) is different compared with the others, losing first one 2-AP molecule, whereas in the case of the others the first escaping species is water. This is in accordance with the coordination in the complexes, which can be concluded certainly on the basis of the crystal structure only. The results of the mass spectrometric behaviour of the complexes support the opinion about their thermal decomposition and instability. The presented escaping order of the ligand molecules is in agreement with the equivalent anisotropic temperature parameters.[15,36]

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