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Cobalt(II), Nickel(II) and Copper(II) Complexes of 4,9-Dimethyl-5,8-diaza-dodeca-2,11-dione Dihydrazone

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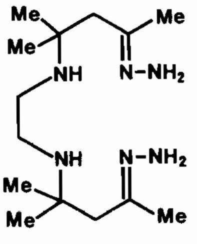
The preparations and properties of 4,9-dimethyl-5,8-diazadodeca-2,11-dione dihydrazone, amhy, as the dihydroperchlorate salt, [amhyH_2](ClO_4), and of the complexes [Co(amhy)(NO_2)]$ClO_4\cdot3/2H_2O$, [Ni(amhy)]ClO_4)$_2$, [Ni(amhy)A]ClO_4, A = NO_2^-, NO_3^-, $CH_3CO_2^-$, ½$C_2O_4^{2-}$, N_3^-, [Ni(amhy)(NCS)$_2$], [Cu(amhy)](ClO_4)$_2$, [Cu(amhy)(NCS)]ClO_4 and [Cu(amhy)]$NO_2\cdot ClO_4$ are reported. An improved preparation of the dihydroperchlorate of 4,9-dimethyl-5,8-diazadodeca-2,11-dione, [amketH_2](ClO_4)$_2$, by reaction of ethane-1,2-diamine dihydroperchlorate with acetone is described and the analogous preparation of [amketH_2](BF_4)$_2$ is reported.

Introduction

The preparation of 4,4,9,9-tetramethyl-5,8-diaza-dodeca-2,11-dione (amket) as the dihydroperchlorate has been reported [1]. Complexes of nickel(II) and copper(II) with the tetradentate diimine of amket are formed by reaction with the metal-ion ammine complexes [1], and of fourteen, fifteen and sixteen membered macrocyclic diamine-diimine ligands by reaction with the complexes of 1,2- [1], 1,3- [1], and 1,4-diamines [2], respectively. The preparations of salts of [3], copper(II) [4], nickel(II) [5] and zinc(II) [4] complexes of the dioxime of amket have been described. The structure of a dinuclear copper(II) complex of the dioxime has been determined by X-ray crystallography [4]. Formation constants of the dioxime with Cu(II) [4, 6] and with Fe(II), Co(II), Ni(II) and Zn(II) [5] and of amket with Cu(II) [6] have been reported.

In this communication the preparation of the dihydrazone of 4,4,9,9-tetramethyl-5,8-diazadodeca-2,11-dione (amhy) as the dihydroperchlorate salt [amhyH_2](ClO_4)$_2$, and the preparation and properties of some complexes of amhy with cobalt(II), nickel(II) and copper(II), are described.



amhy

The reported preparation of [amketH_2](ClO_4)$_2$ is by the sequence of reactions shown in Scheme 1 [1]. This reaction requires separation of the 4,11- and 4,14-diene isomers of the nickel(II) macrocycle complex by fractional crystallisation, the required 4,14-diene isomer occurring in about 33% yield when tris(ethane-1,2-diamine)nickel(II) perchlorate reacts with acetone at room temperature [7]. This separation may be avoided by using the slower reaction of tris(ethane-1,2-diamine)nickel(II) nitrate with acetone, which yields predominantly the complex of the 4,14-diene macrocycle [7]. Evne so, the preparation of [amketH_2](ClO_4)$_2$ by this procedure is tedious, and a much improved single step preparation is now reported.

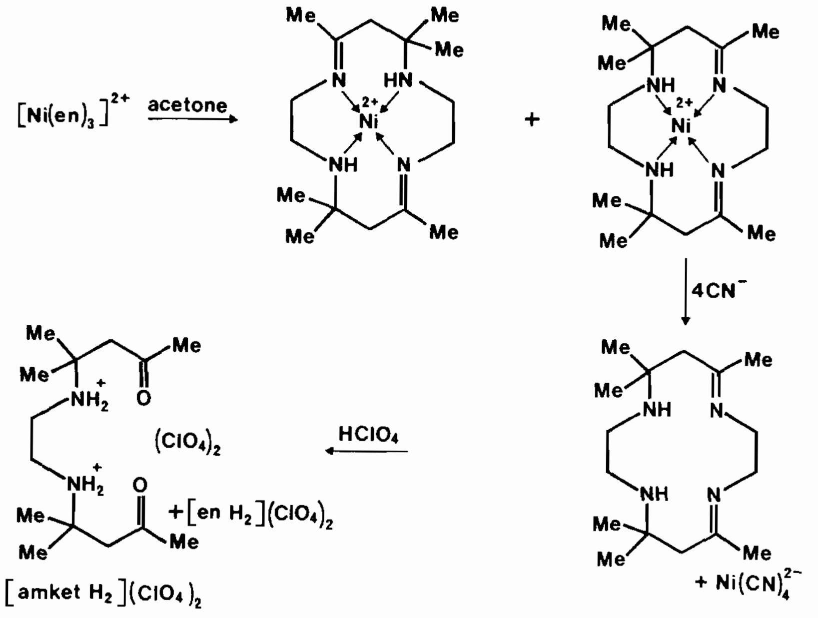
Mono-protonated salts of ethane-1,2-diamine, with a variety of large anions (*e.g.* ClO_4^-, BF_4^-, Br^-, CNS^-) react rapidly with acetone to form salts of the diprotonated 4,11-diene macrocycle in high yield [8], as shown in Scheme 2.

Diprotonated salts of ethane-1,2-diamine, with appropriate anions, also react rapidly with acetone to form di-N-isopropylidene ammonium salts, which may crystallise from concentrated solutions. A much slower reaction, which is now reported, follows on to yield amket which crystallises as the sparingly soluble dihydroperchlorate, or as the dihydrotetrafluoroborate salt, Scheme 3.

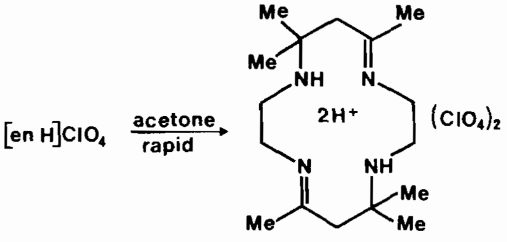
Experimental

4,4,9,9-Tetramethyl-5,8-diazoniumdodec-2,11-dione diperchlorate, [amketH$_2$](ClO_4)$_2$ [1] (Note 1)

Ethane-1,2-diamine (20 g) was added to acetone (300 ml) in a 500 ml flask, and the solution cooled



scheme 1



scheme 2

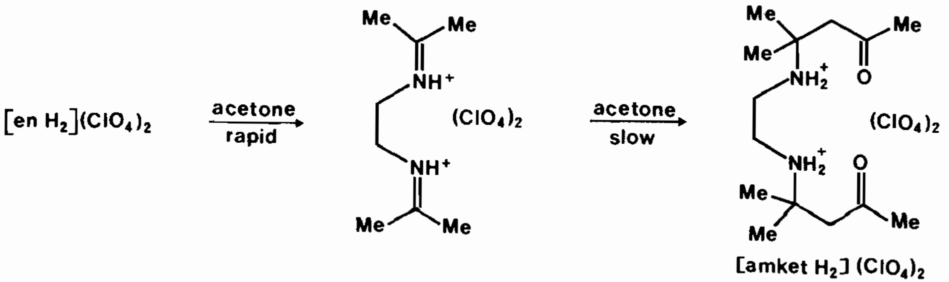
in an ice bath. Perchloric acid (72% 1:1.95 mol. propn, *ca.* 50 ml, Note 2) was added dropwise with stirring, keeping the temperature below 20 °C (Note 3). The flask was completely filled with acetone, stoppered (Note 4) and left without agitation (Note 5). After several hours, fine crystals of the product, which is very insoluble in acetone, commenced to separate, and continued to form for weeks, the bulk of the product being present after 10 days. The product was filtered off, washed with acetone until the washings were colourless, and air dried. Yield 85%. Alternatively, ethane-1,2-diamine dihydroperchlorate (Note 6) was dissolved in acetone, 0.025 mol propn of ethane-1,2-diamine added, and the preparation continued as above, with similar yield.

Notes

1: The product is not shock sensitive, and decomposed nonviolently when heated, but should still be treated with the caution due to any amine hydroperchlorate.

2: The exact quantity of acid required was determined by a prior titration of the diamine by the acid, in water. The slight excess of amine over the stoichiometric quantity greatly accelerates the reaction.

3: If the temperature is allowed to rise, the amount of brown tarry byproduct is increased. In addition, 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene dihydroperchlorate may crystallise as the system passes the 'half neutralisation' region. This will eventually redissolve to form the desired product.



scheme 3

4: Exclusion of air reduces the amount of tarry byproduct.

5: Agitation may cause excessive nucleation of the product which leads to a very finely divided material, which is extremely difficult to filter and wash. The product may nucleate during the latter part of the neutralisation reaction, particularly if the flask has been previously used for the reaction and not carefully cleaned. This does not matter, except that the product is difficult to filter and wash.

6: Ethane-1,2-diamine dihydroperchlorate may detonate violently if heated.

4,4,9,9-Tetramethyl-5,8-diazoniumdodeca-2-11-dione Ditetrafluoroborate, [amketH$_2$](BF$_4$)$_2$

The preparation was carried out as for the perchlorate, using ethane-1,2-diamine plus tetrafluoboric acid, or ethane-1,2-diammonium tetrafluoroborate. Yield *ca.* 80%. A sample for analysis was recrystallised from hot methanol. *Anal.* Found: C, 38.4; H, 6.7%. Calcd. for $C_{14}H_{30}B_2F_8N_2$, C, 38.7; H, 7.0%.

4,4,9,9-Tetramethyl-5,8-diazadodeca-2,11-dione Dihydrazone Dihydroperchlorate, [amhyH$_2$](ClO$_4$)$_2$

[amketH$_2$](ClO$_4$)$_2$ was stirred with a cold aqueous solution containing a small excess of hydrazine monohydroperchlorate (prepared from hydrazine hydrate and one mol. propn. of perchloric acid). The white crystalline product was filtered off after 12 h, washed with cold water and dried. Yield 75%. The compound was recrystallised from acetonitrile/propan-2-ol for analysis. *Anal.* Found: C, 34.7; H, 7.1; N, 17.7%. Calcd. for $C_{14}H_{34}Cl_2N_6O_8$, C, 34.7; H, 7.1; N, 17.4%.

(4,4,9,9-Tetramethyl-5,8-diazadodeca-2,11-dione Dihydrazone)nickel(II) Perchlorate, [Ni(amhy)](ClO$_4$)$_2$

Nickel(II) perchlorate hydrate (20 g) was dissolved in water (100 ml) and hydrazine hydrate (15 ml, 6 mol. propn) was added, followed by [amketH$_2$](ClO$_4$)$_2$ (24 g, 0.96 mol. propn). The mixture was stirred until the [amketH$_2$](ClO$_4$)$_2$ dissolved. The colour of the solution gradually changed from blue to red, and the orange *product* crystallised. After several hours the solution was cooled in ice and the product was filtered off and washed with several small portions of ice-water. Yield *ca.* 24 g, 80%. For preparative purposes the product can be used without purification, but it can be recrystallised from hot 1:1 water:methanol, or from hot acetonitrite/propan-2-ol. The compound was also formed by reacting [amhyH$_2$](ClO$_4$)$_2$ with nickel acetate tetrahydrate in methanol *Anal.* Found: C, 31.2; H, 5.9; N, 15.7; Ni, 10.4%; calcd. for $C_{14}H_{32}Cl_2N_6NiO_8$, C, 31.0; H, 6.0; N, 15.5; Ni, 10.8%. Infrared: ν(NH), 3385w, 3300m, 3200s; ν(C=N), 1670; δ(NH$_2$), 1590 cm^{-1}.

CAUTION: It is *essential* that water be used as solvent for this reaction, since extremely shock sensitive nickel(II) hydrazine perchlorate compounds may crystallise from other solvents. No problems have occured with the preparation as described, but the system should be regarded as potentially dangerous, and the final filtrate disposed of carefully.

Attempts to induce [Ni(amhy)](ClO$_4$)$_2$, or any of the other complexes of amhy, to explode by shock or heating were unsuccessful, but they should all be treated as potentially hazardous.

Trans-*di-N-thiocyanato-(4,4,9,9-Tetramethyl,5,8-diazadodeca-2,11-dione Dihydrazone)nickel(II) Hemihydrate,* trans-*[Ni(amhy)(NCS)$_2$]·½H$_2$O*

Sodium thiocyanate was added to a hot aqueous solution of [Ni(amhy)](ClO$_4$)$_2$. The sparingly soluble blue *product* was filtered off from the cold solution and recrystallised from hot water. *Anal.* Found: C, 41.0; H, 7.0; N, 24.0; Ni, 12.5%; Calcd. for $C_{32}H_{66}N_{16}Ni_2OS_4$, C, 41.0; H, 7.0; N, 23.9; Ni, 12.5%. Infrared: ν(LH), 3500; ν(NH), 3370, 3265, 3230; ν(C≡N), 2085m, 2060vs; ν(C=N), 1630; δ(NH$_2$), 1600sh cm^{-1}. *d–d* (reflectance): 10200, 16800, 26700 cm^{-1}. (Acetone: 10200 (ϵ = 6 mol^{-1} m^2), 17200(6), 27700(20) cm^{-1}.

Analysis favours the hemi-hydrate formulation, but the structural study [9] characterised the compound as a mono-hydrate. Possibly different hydrates can be prepared.

O,O'-Nitrato-(4,4,9,9-Tetramethyl-5,8-diazadodeca-2,11-dione Dihydrazone)nickel(II) Perchlorate Hydrate, [Ni(amhy)(NO$_3$)]ClO$_4$·H$_2$O

[Ni(amhy)](ClO$_4$)$_2$ was dissolved in a hot aqueous solution of sodium nitrate. The moderately soluble blue *product* was filtered off from the cold solution and recrystallised from hot water. *Anal.* Found: C, 32.0; H, 6.5; N, 18.5; Ni 11.3%; Calcd. for $C_{14}H_{34}ClN_7NiO_8$, C, 32.3; H, 6.6; N, 18.8; Ni, 11.2%. Infrared: ν(OH), 3590, 3515; ν(NH), 3415, 3390, 3290, 3270, 3205; ν(C=N) + δ(NH$_2$), 1620; ν_3(NO$_3^-$), 1485, 1270; ν_2(NO$_3^-$) 805 cm^{-1}. *d–d* (reflectance): 10800, 17200, 27200 cm^{-1}.

O,O'-Nitrito-(4,4,9,9-Tetramethyl-5,8-diazadodeca-2,11-dione Dihydrazone)nickel(II) Perchlorate Monohydrate, [Ni(amhy)(NO$_2$)]ClO$_4$·H$_2$O

Sodium nitrite was added to a hot aqueous solution of [Ni(amhy)]ClO$_4$)$_2$ and the sparingly soluble blue *product* was filtered off from the cold solution and recrystallised from hot water. *Anal.* Found: C, 33.3; H, 6.8; Ni, 11.5%. Calcd. for $C_{14}H_{34}ClN_7NiO_7$, C, 33.2; H, 6.8; Ni, 11.6%. Infrared: ν(OH), 3590, 3515; ν(NH), 3300w, 3280, 3215; ν(C=N) + δ(NH$_2$), 1625 cm^{-1}. *d–d* (reflectance): 8400(sh), 10600, 17200, 27000 cm^{-1}.

Analysis favours the monohydrate formulation, and hydration is supported by the infrared spectrum. The structural study of crystals, grown from a non-aqueous solvent system, revealed a non-hydrated form [9].

O,O′-Acetato-(4,4,9,9-Tetramethyl-5,8-diazadodeca-2,11-dione Dihydrazone)nickel(II) Perchlorate, $[Ni(amhy)(CH_3CHOO)]ClO_4$

$[Ni(amhy)](ClO_4)_2$ was dissolved in a hot concentrated aqueous solution of sodium acetate. The appreciably soluble blue *product* was filtered off from the cold solution and recrystallised from hot methanol/propan-2-ol. *Anal.* Found: C, 38.2; H, 6.8; Ni, 11.6%. Calcd. for $C_{16}H_{35}ClN_6NiO_6$, C, 38.3; H, 7.0; Ni, 11.7%. Infrared: ν(NH), 3395, 3365, 3310, 3270, 3240; ν(C=N), 1650w; $\delta(NH_2)$, 1622; CH_3COO^- ν_{as}(OCO), 1545; ν_s(OCO), 1450; δ(OCO), 675 cm^{-1}. *d–d* (reflectance): 10500, 168000, 27000 cm^{-1}, μ_{eff} (298 K), 3.10 B.M.

μ-Oxalato bis-(4,4,9,9-Tetramethyl-5,8-diazadodeca-2,11-dione Dihydrazone)dinickel Perchlorate, $[\{Ni(amhy)\}_2C_2O_4](ClO_4)_2$

Sodium oxalate was added to a hot aqueous solution of $[Ni(amhy)](ClO_4)_2$ and the sparingly soluble blue *product* was filtered off from the cold solution and recrystallised from hot acetonitrile/propan-2-ol. *Anal.* Found: C, 37.3; H, 6.5; Ni, 11.8%. Calcd. for $C_{30}H_{64}Cl_2N_{12}NiO_{12}$, C, 37.0; H, 6.6; Ni, 12.1%. Infrared: ν(NH), 3378, 3278, 3263; ν_{as}(OCO), 1650vs; ν_s(OCO), 1305; δ(OCO), 795 cm^{-1}. *d–d* (reflectance): 10400, 17000, 27400 cm^{-1}.

Di-μ-azidobis-(4,4,9,9-Tetramethyl-5,8-diazadodeca-2,11-dione Dihydrazone)dinickel Perchlorate Trihydrate, $[\{Ni(amhy)N_3\}_2](ClO_4)_2\cdot 3H_2O$

Sodium azide was added to a hot aqueous solution of $[Ni(amhy)](ClO_4)_2$; the moderately soluble light blue *product* was filtered off from the cold solution and recrystallised from hot water. *Anal.* Found: C, 33.0; H, 7.3; N, 24.3; Ni, 11.4%. Calcd. for $C_{28}H_{70}Cl_2N_{18}Ni_2O_{11}$, C, 32.9; H, 6.9; N, 24.6; Ni, 11.5%. Infrared: ν(OH) 3600; ν(NH), 3440, 3400, 3380, 3290, 3230; N_3^-, 2122, 2090vs, 2010; ν(C=N), 1645; $\delta(NH_2)$, 1600br,sh cm^{-1}. *d–d* (reflectance): 10000, 16200, 2700(br) cm^{-1}.

(4,4,9,9-Tetramethyl-5,8-diazadodeca-2,11-dione Dihydrazone)copper(II) Perchlorate, $[Cu(amhy)](ClO_4)_2$

$[Ni(amhy)](ClO_4)_2$ was dissolved in the minimum volume of hot methanol/water (1:1), and a slight excess of copper(II) perchlorate was added. The solution was quickly filtered and cooled by vacuum evaporation. The dark blue *product* was filtered from the cold solution and recrystallised from hot water/methanol. If the preparation solution is heated the crimson condensation product of $[Cu(amhy)]^{2+}$ with acetone may be formed by partial hydrolysis of the amhy. The compound was also formed by reacting $[amhyH_2](ClO_4)_2$ with copper(II) acetate hydrate in methanol. *Anal.* Found: C, 30.9; H, 5.9; Cu 12.1; N, 15.5%. Calcd. for $C_{14}H_{32}Cl_2CuN_6O_8$, C, 30.7; H, 5.9; Cu, 11.6; N, 15.4%. Infrared: ν(NH), 3365, 3300(w), 3205; ν(C=N), 1650; $\delta(NH_2)$, 1600(sh) cm^{-1}. μ_{eff} (298 K), 1.82 B.M.

(4,4,9,9-Tetramethyl-5,8-diazadodeca-2,11-dione Dihydrazone)copper(II) Nitrite Perchlorate Hemihydrate, $[Cu(amhy)]NO_2\cdot ClO_4\cdot ½H_2O$

This quite soluble blue *compound* was prepared as for the nickel(II) compound and recrystallised from hot methanol/propan-2-ol. *Anal.* Found: C, 33.1; H, 7.1; N, 19.4%; Calcd. for $C_{28}H_{66}Cl_2Cu_2N_{14}O_{13}$, C, 33.5; H, 6.6; N, 19.5%. Infrared: ν(OH), 3605; ν(NH), 3370, 3270, 3210; ν(C=N), 1670; $\delta(NH_2)$, 1630 cm^{-1}.

Thiocyanato-(4,4,9,9-Tetramethyl-4,8-diazadodeca-2,11-dione Dihydrazone)copper(II) Perchlorate, $[Cu(amhy)](CNS)ClO_4$

Desiccated sodium thiocyanate was added to $[Cu(amhy)](ClO_4)_2$ in a small volume of acetonitrile (2:1 mol. propns) followed by propan-2-ol. The blue *solid* which crystallised was filtered off and recrystallised from acetonitrile/propan-2-ol. The compound is unstable in water. *Anal.* Found: C, 35.6; H, 6.4; N, 19.4%. Calcd. for $C_{15}H_{32}ClCuN_7O_4S$, C, 35.8; H, 6.2; N, 19.5%. Infrared: ν(NH), 3378, 3305, 3225; ν(C≡N), 2058vs; ν(C=N), 1650; $\delta(NH_2)$, 1620br,sh cm^{-1}.

O,O′-Nitrito-(4,4,9,9-Tetramethyl-4,8-diazadodeca-2,11-dione Dihydrazone)cobalt(II) Perchlorate Sesquihydrate, $[Co(amhy)(NO_2)]ClO_4\cdot 3/2H_2O$

The preparation of $[Ni(amhy)](ClO_4)_2$ was followed, substituting cobalt(II) perchlorate for the nickel(II) salt. Sodium nitrite (20 g) was added to the resulting pink solution; the sparingly soluble pink *product* crystallised and was filtered off and recrystallised from hot water. *Anal.* Found: C, 32.5; H, 6.9; Co, 11.3%. Calcd. for $C_{28}H_{70}Cl_2Co_2Cl_2N_{14}O_{15}$, C, 32.6; H, 6.8; Co, 11.4%. Infrared: ν(OH), 3560, 3440; ν(NH), 3400, 3420, 2410, 3360, 3270; ν(C=N), 1650; $\delta(NH_2)$, 1606 cm^{-1}.

Results and Discussion

Metal-ion Compounds of 4,4,9,9-Tetramethyl-5,8-diazadodeca-2,11-dione Dihydrazone

Compounds of Nickel(II)

Orange, singlet ground state $[Ni(amhy)](ClO_4)_2$ was formed by reaction of $[amhyH_2](ClO_4)_2$ with nickel(II) acetate in methanol. It was more conveniently prepared by reaction of $[amketH_2](ClO_4)_2$, nickel(II) perchlorate and hydrazine in water.

The *d–d* spectrum of the compound as the solid, or in solution in poorly coordinating solvents such as acetone, shows a single band at 22000 cm^{-1}, typical of compounds with the singlet ground state NiN$_4$ chromophore. In solvents with better coordinating ability, it forms blue-violet solutions, with spectra typical of octahedral, triplet ground state nickel(II), (*e.g.* in CH$_3$CN, 11600, 18600 and 28000 cm^{-1}). It is sparingly soluble in water, the spectrum showing bands of both singlet ground state (*ca.* 20000 cm^{-1}) and triplet ground state (*ca.* 10300 17000, 28000 cm^{-1}) species. It is more soluble in water in the presence of salts of a variety of oxyanions, forming blue-violet solutions. From a number of these solutions blue-violet triplet ground state compounds of type [Ni(amhy)A]ClO$_4$, where A = NO$_2^-$, NO$_3^-$, CH$_3$COO$^-$, ½C$_2$O$_4^{2-}$, crystallised. These have infrared spectral bands assignable to the anions typical of compounds of known symmetrical chelate structures, *e.g.* the bis(ethane-1,2-diamine)-nickel(II) analogues [10–14]. For [Ni(amhy)(NO$_2$)]-ClO$_4$ a structure of this type has been confirmed by X-ray crystallography [9]. The *d–d* spectra of the compounds with coordinated oxyanions (Experimental) are all very similar, and as expected for *cis*-NiN$_4$O$_2$ chromophores. A compound [Ni(amhy)N$_3$]-ClO$_4$ crystallised from solutions containing azide, and this is assigned a dinuclear structure [{Ni(amhy)-N$_3$}$_2$](ClO$_4$), as reported for the analogous compound formed by 2,2′,2″-triaminotriethylamine [15]. Sparingly soluble blue-violet Ni(amhy)(NCS)$_2$·H$_2$O which crystallised from solutions containing thiocyanate has been shown by X-ray crystallography to have an octahedral structure with *trans* nitrogen coordinated thiocyanate [9].

Copper(II)

Copper(II) perchlorate, [H$_2$amket](ClO$_4$)$_2$, and hydrazine react in water to form dark blue [Cu(amhy)](ClO$_4$)$_2$, although reduction of some of the copper(II) by the hydrazine causes complications, and the yield is low. The compound is more conveniently prepared by the reaction of [amhyH$_2$]-(ClO$_4$)$_2$ with copper(II) acetate in methanol, or by substitution of copper(II) for nickel(II) in [Ni(amhy)](ClO$_4$)$_2$, which occurs rapidly in aqueous solution.

The colour of solutions of [Cu(amhy)](ClO$_4$)$_2$ depends on the coordinating ability of the solvent, ranging from blue in acetone (band at 17100 cm^{-1}) to purple in water (band at 16300 cm^{-1}). The reflectance spectrum of the dark blue solid has a band at 16200 cm^{-1}, suggesting that axial interactions are present, possibly with the terminal –NH$_2$ groups of other amhy ligands. The spectrum also shows a strong band in the near ultra-violet (*ca.* 25000 cm^{-1}) which is absent from the spectra in solution (or from the spectrum of [Cu(amhy)]NO$_2$·ClO$_4$, below), which accounts for the dark-blue colour. Bands in this region are often observed for di- and poly-nuclear copper(II) compounds.

The compound [Cu(amhy)]NO$_2$·ClO$_4$ is much more soluble in water than the nickel(II) or cobalt(II) analogues. The blue solid (reflectance, 15700 cm^{-1}) forms green solutions in acetone, and acetonitrile, (acetone, 13300 cm^{-1} ϵ, 22 mol^{-1} m^2) which indicates some structural difference between the solid and solution, probably coordination of the nitrite ion in solution. The bands of the infrared spectra of the nitrite compounds assignable as ν_{as}(NO) and ν_s(NO) of the nitrite ion cannot be assigned unambiguously because of strong amhy bands in the region. However the spectrum of the copper(II) compound is clearly different from that of the nickel(II) compound of known symmetrical chelate structure, and the most probable nitrite band assignment (ν_{as} 1350, ν_s 1230, δ 805 cm^{-1}) is more typical of ionic nitrite (NaNO$_2$, 1335, 1250, 830 cm^{-1}). The compound is therefore formulated with non-coordinated nitrite, although coordination of the nitrite ion apparently occurs in solution in non-aqueous solvents.

Addition of thiocyanate to solutions of [Cu(amhy)](ClO$_4$)$_2$ resulted in a colour change to green, and a blue-green solid [Cu(amhy)(NCS)]-ClO$_4$ was isolated. The bands of the reflectance spectrum (13300, 25500 cm^{-1}) and the ν(C≡N) band of the infrared spectrum (2060 cm^{-1}) are indicative of coordination of the thiocyanate. The compound forms a blue-green solution in organic solvents (acetone: charge transfer, 26400 cm^{-1}; ϵ 24 mol^{-1} m^2; *d–d* 13200 cm^{-1}, ϵ, 7.6 mol^{-1} m^2) and the similarity of the spectrum to that of the solid indicates coordination of the thiocyanate in solution. The addition of azide to solutions of the perchlorate caused similar colour changes in solution, but no solid was isolated.

Cobalt(II)

Cobalt(II) perchlorate, [H$_2$amket](ClO$_4$)$_2$ and hydrazine react in aqueous solution to form a pink solution, but the simple perchlorate salt of the product is very soluble. The only compound isolated for cobalt(II) was sparingly soluble pink [Co(amhy)-(NO$_2$)]ClO$_4$·3/2H$_2$O.

The *d–d* spectrum of the solid (reflectance, *ca.* 7900, 12000, 19400 cm^{-1}, 21000 sh) and solutions (acetone, 7200 (0.8); 11200 (0.6); 25700 (3.2) (ϵ, mol^{-1} m^2)) are similar, and compatible with octahedrally coordinated, quartet ground state cobalt(II). The effective magnetic moment is 4.90 B.M., supporting this assignment. The nitrite bands in the infrared spectrum are difficult to assign because of amhy bands, but the spectrum is similar to that of the nickel(II), rather than of the copper(II) analogue, so the compound is formulated with chelate nitrite.

Attempts to oxidise the compound to cobalt(III) were not successful. The cobalt(II) complex of the dioxime of amket forms a non-labile dinuclear oxygen adduct when exposed to oxygen [16].

General

The molecule amhy coordinates as a tetradentate ligand in both planar (*e.g.* *trans*-[Ni(anhy)(NCS)$_2$]-H_2O) and folded (*e.g.* [Ni(amhy)(NO$_2$)ClO$_4$) configurations. With nickel(II), both singlet ground state, square planar [Ni(amhy)](ClO$_4$)$_2$ and triplet ground state, octahedral, compounds were isolated, the latter generally with sterically non-demanding additional ligands. The complexes with cobalt(II), nickel(II) and copper(II) are stable in cold water, but are slowly hydrolysed in hot water as amhy degrades to ethanediamine, hydrazine and 4-methylpent-3-ene-2-one (mesityloxide). Hydrolysis is rapid in acid solution, and is also accelerated by base. The non-coordinated NH_2 groups of the amhy complexes could, in principle, coordinate to other metal-ions, but attempts to isolate such derivatives were not successful. These NH_2 groups are reactive towards molecules with carbonyl functions and compounds formed by such reactions will be described subsequently.

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