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TRANSITION METAL NITRATE COMPLEXES OF 1,4,5-TRIAZANAPHTHALENE

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ABSTRACT

Coordination compounds of some first row transition metal nitrates with 1,4,5-triazanaphthalene (pyrido[2,3-*b*]pyrazine), abbreviated tnp, have been prepared and characterized by thermal analysis, infrared, visible and near-infrared spectra, and magnetic susceptibility. The compounds have the formulas $Co(tnp)(NO_3)_2$, $Ni(tnp)(NO_3)_2 \cdot H_2O$, $Cu(tnp)_2(NO_3)_2$, and $Zn(tnp)(NO_3)_2$. The infrared spectra identify the nitrate groups as functioning as bidentate ligands. The absorptions in the TGA and DSC appear in the same temperature ranges. The major decompositions correspond to simultaneous loss of ligand and decomposition of the nitrate groups leaving an oxide as the residue.

INTRODUCTION

Coordination compounds of cobalt(II), nickel(II), copper(II), and zinc(II) with heterocyclic amines as ligands have been a fruitful area for research. The complexes of pyridine and substituted pyridines predominate but amines derived from the naphthalene structure have also been used. The anion associated with the metal(II) ion is usually chloride ion which can function as a monodentate ligand. The nitrate ion is usually noncoordinating but when functioning as a ligand it is a weaker ligand than chloride ion and it can function as either a monodentate or a bidentate ligand.

Underhill has reported complexes of quinoxalene (or 1,4-diazanaphthalene) and substituted quinoxalenes with copper(II) nitrate and with nickel(II) nitrate [1–3]. There are variety of complexes of 1,8-diazanaphthalene (or

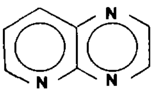

Fig. 1. 1,4,5-Triazanaphthalene, abbreviated tnp.

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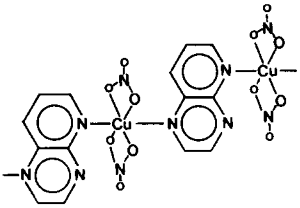

Fig. 2. The proposed structure of Cu(tnp)$(NO_3)_2$.

1,8-naphthyridine) including some where the metal ion is eight coordinate [4–6]. Transition metal chloride complexes of 1,5-diazanaphthalene are polymeric with both bridging 1,5-diazanaphthalene molecules and bridging chloride ions [7]. The ligand discussed in this paper, 1,4,5-triazanaphthalene or pyrido[2,3-*b*]pyrazine (see Fig. 1), has been less widely studied. Complexes with transition metal chlorides appear to be similar to those of 1,5-diazanaphthalene [8]. A copper(II) nitrate complex of 1,4,5-triazanaphthalene was found to contain bridging 1,4,5-triazanaphthalene ligands with nitrate ions functioning as bidentate ligands as shown in Fig. 2 [9].

Thermal analysis data of transition metal complexes of aromatic amines have been reported primarily for thiocyanate and related anions. For example, $[Co(pyridine)_4(NCS)_2]$ loses its pyridine ligands stepwise followed by further decomposition eventually leading to CoO [10]. Some thermal analysis data have been presented for complexes of substituted imidazoles, including those of $Cu(NO_3)_2$, $Co(NO_3)_2$, and $Ni(NO_3)_2$ [11]. Numerous studies of the thermal decomposition of metal nitrates in the absence of ligands other than water have been reported including a report on the effect of experimental conditions [12–15].

This paper reports the synthesis and characterization of complexes of 1,4,5-triazanaphthalene (abbreviated tnp) with some first row transition metal nitrates. The methods of characterization include infrared and visible spectroscopy, magnetic susceptibility, and thermal analysis.

EXPERIMENTAL

Synthesis

1,4,5-Triazanaphthalene was prepared from commercial 2,3-diaminopyridine and glyoxal sodium bisulfite by the method of Leese and Raydon [16]. The complexes were prepared by mixing 50 ml equimolar portions (4–7 mmol) of the metal nitrate and the ligand, each in absolute ethanol. The copper(II) complex precipitated immediately. For the other metals it was necessary to reduce the volume of solution in vacuo to obtain precipitation.

Color, magnetic susceptibility, analysis

1,4,5-Triazanaphthalene, $C_7H_5N_3$. Calc.: C, 64.1; H, 3.8; N, 32.0. Found: C, 64.0; H, 3.5; N, 35.6.

Co(tnp)$(NO_3)_2$, $CoC_7H_5N_5O_6$. Purple solid. 4.46 B.M. Calc.: C, 26.8, H, 1.60; N, 22.3; Co, 18.8. Found: C, 27.9; H, 1.56; N, 23.5; Co, 18.6.

Ni(tnp)$(NO_3)_2 \cdot H_2O$, $NiC_7H_7N_5O_7$. Green solid. 3.18 B.M. Calc. C, 25.3; H, 2.13; N, 21.1; Ni, 17.7. Found: C, 27.4; H, 2.21; N, 21.8; Ni, 17.0.

Cu$(tnp)_2(NO_3)_2$, $CuC_{14}H_{10}N_8O_6$. Blue solid. 1.73 B.M. Calc. C, 37.4; H, 2.24; N, 24.9; Cu, 14.1. Found: C, 37.1; H, 2.37; N, 25.9; Cu, 14.4.

Zn(tnp)$(NO_3)_2$, $ZnC_7H_5N_5O_6$. Off-white solid. Calc. C, 26.2; H, 1.60; N, 21.8; Zn, 20.4. Found: C, 25.1; H, 1.96; N, 22.0; Zn, 20.9.

Instrumentation

Infrared spectra were obtained as nujol mulls and by reflectance using a Nicolet 5DX FTIR spectrophotometer in the 4000–400 cm^{-1} region and as nujol mulls between polyethylene plates on a Perkin-Elmer Model 621 spectrophotometer in the 400–200 cm^{-1} range. Visible and near-infrared spectra were obtained on a Cary 14 at room temperature and at liquid nitrogen temperature as Halocarbon mulls as previously described [17]. Magnetic susceptibility measurements were obtained at room temperature by the Gouy method using the apparatus previously described [7]. The thermal analyses were performed on a Du Pont 1090 thermal analyzer under nitrogen at a flow rate of 25 ml min^{-1} with a heating rate of 10°C min^{-1} for the TGA and 5° min^{-1} for the DSC.

RESULTS

Infrared spectra

The infrared spectrum of the 1,4,5-triazanaphthalene agrees well with that reported [18]. The ligand absorptions in the complexes are similar to the free ligand except for a general shift to higher energies as expected [7]. New absorptions appear due to the NO_3 group; the important bands are listed in Table 1 and the combination bands are also shown in Fig. 3 Bands due to the NO_3 group below 1600 cm^{-1} are useful in distinguishing between ionic and covalent nitrate. Ionic nitrate has D_{3h} symmetry and the assignments

TABLE 1

Infrared bands due to coordinated nitrate

Vibrational mode	Co(tnp)$(NO_3)_2$	Ni(tnp)$(NO_3)_2$ $\cdot H_2O$	Cu$(tnp)_2(NO_3)_2$	Zn(tnp)$(NO_3)_2$
NO_2 symmetrical stretch (cm^{-1})	1279	1272	1274	1292
NO stretch (cm^{-1})	1021sh, 1014	1023	1017	1019
Nonplanar rock (cm^{-1})	805	815, 804	806	812
Combination (cm^{-1})	1776, 1718	1776, 1719	1760, 1720	1775, 1720

are $\nu_1 = 1050$ cm^{-1} (N–O stretch, infrared-inactive), $\nu_2 = 831$ cm^{-1} (NO_2 deformation), $\nu_3 = 1390$ cm^{-1} (NO_2 asymmetric stretch), and $\nu_4 = 720$ cm^{-1} (planar rock) [19]. In complexes where the nitrate group is covalently bound to the metal, the symmetry is lowered to C_{2v} which results in significant changes in the number and positions of the absorptions [19,20]. The N–O stretch becomes infrared-active and appears in the range 970–1034 cm^{-1}. The NO_2 deformation becomes a nonplanar rock and appears in the range 780–810 cm^{-1}. The NO_2 asymmetric stretch is split into two bands, one between 1480 and 1530 cm^{-1} and the other between 1250 and 1290 cm^{-1}. However, it is not possible to distinguish monodentate from bidentate coordination from these bands [20] but the distinction can be made with the combination bands near 1750 cm^{-1} [21]. There are other combination bands near 2400 cm^{-1} and an overtone of the symmetric stretching vibration is near 2000 cm^{-1}. The bands near 1750 cm^{-1} are generally clearly defined and relatively strong in comparison to those near 2000 and 2400 cm^{-1}. The magnitude of the splitting of the bands near 1750 cm^{-1} depends on the metal–nitrate interaction; it is generally larger for bidentate than for monodentate coordination for a given metal and oxidation state. The separation for monodentate nitrate coordination is in the range 5–26 cm^{-1} while for

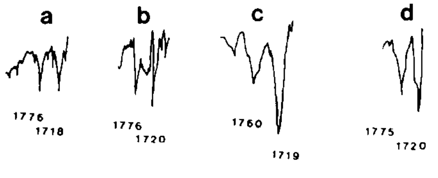

Fig. 3. Combination bands of the coordinated NO_3 group. (a) Co(tnp)$(NO_3)_2$, (b) Ni(tnp)$(NO_3)_2 \cdot H_2O$, (c) Cu$(tnp)_2(NO_3)_2$, (d) Zn(tnp)$(NO_3)_2$.

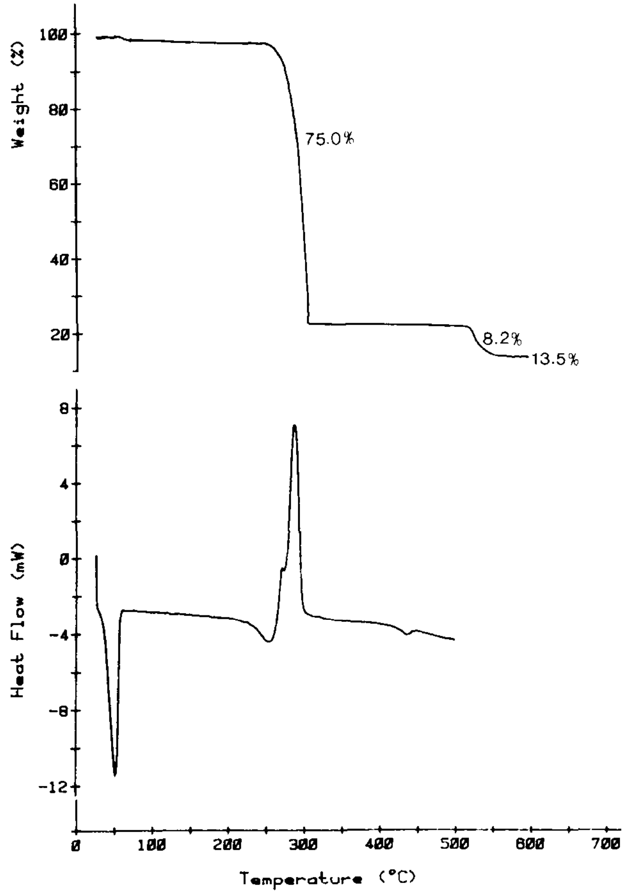

Fig. 4. Thermal analysis of Co(tnp)$(NO_3)_2$.

bidentate coordination it is 20–66 cm^{-1}. Ionic nitrates, when present, give rise to a single sharp, narrow band in this region.

Thermal analysis

The results of the thermal analysis are shown in Figs. 4–7. The cobalt complex shows a mass loss of 75.0% between 280 and 300 °C with an exothermic peak at the same place in the DSC curve. An endothermic peak near 50 °C is probably due to loss of adsorbed water since the complex shows no unusual changes when heated in a glass capillary tube to 100 °C. The residue at 500 °C corresponds to 21.7% of the initial sample. The nickel complex shows a mass loss of 6.1% between 135 and 175 °C and another mass loss of 69.7% between 330 and 350 °C. The DSC has peaks at

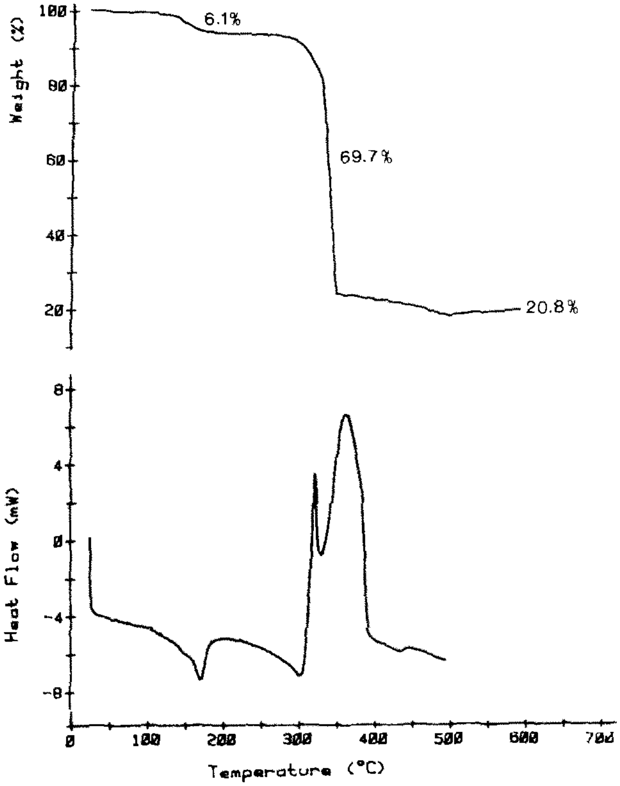

Fig. 5. Thermal analysis of Ni(tnp)$(NO_3)_2 \cdot H_2O$.

corresponding temperatures. The residue at 600°C corresponds to 20.8% of the initial sample. The copper complex shows mass losses of 26.1 and 49.8% at 200–225 and 280–300°C, respectively. The residue at 600°C is 17.6% of the original sample. The DSC has peaks at temperatures corresponding to the mass losses. The zinc complex shows only a single mass loss of 70.0% between 325 and 360°C. The residue at 600°C is 30.0% of the initial sample. The peak in the DSC in the temperature range of the mass loss is endothermic whereas the corresponding decompositions in the other complexes are exothermic.

Visible and near-infrared spectra

Since the visible–near-infrared spectra were obtained as mulls, it was impossible to determine absorptivities. For individual spectra the relative absorbances are comparable within the same spectrum. The cobalt complex, at liquid nitrogen temperature, had absorptions at 8000 and 9710 cm^{-1}, which are in the same envelope but resolved, 14800 cm^{-1}, and 19200 cm^{-1}. The spectrum of the nickel complex, at liquid nitrogen temperature, is

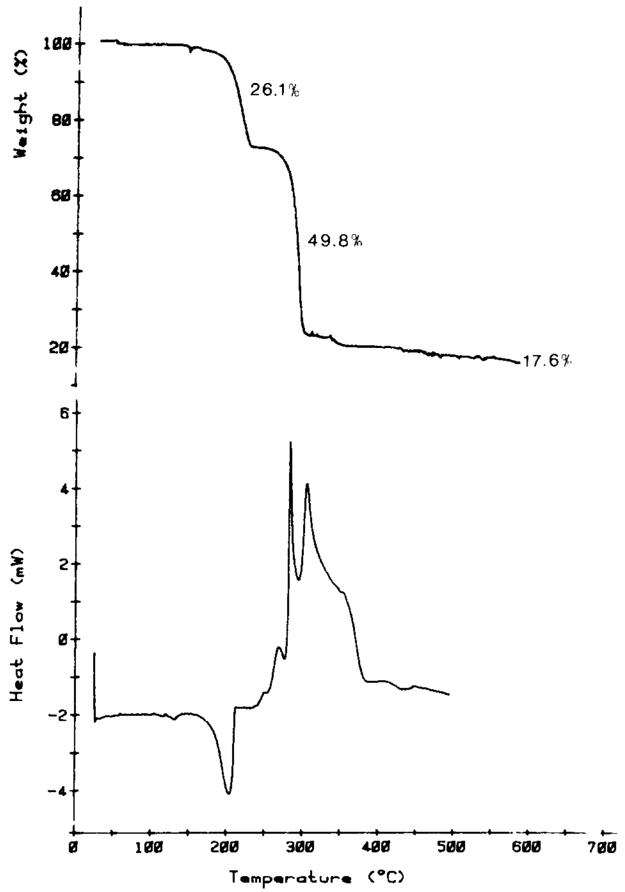

Fig. 6. Thermal analysis of $Cu(tnp)_2(NO_3)_2$.

shown in Fig. 8. It has absorptions at 8050 and 9920 cm^{-1} together resolved as previously reported [17], 13250 cm^{-1} (weak), 16100 cm^{-1}, and 23500 cm^{-1}. The copper complex has a single absorption at 15600 cm^{-1} tailing slightly toward the near-infrared.

DISCUSSION

$Co(tnp)(NO_3)_2$

The visible–near-infrared spectrum of the cobalt complex is similar to those of other octahedral or distorted octahedral complexes [22]. The distortions from regular octahedral symmetry due to the nonequivalences of the ligands make it difficult to assign transitions to the observed absorptions. The magnetic moment of 4.46 B.M. at room temperature is somewhat low

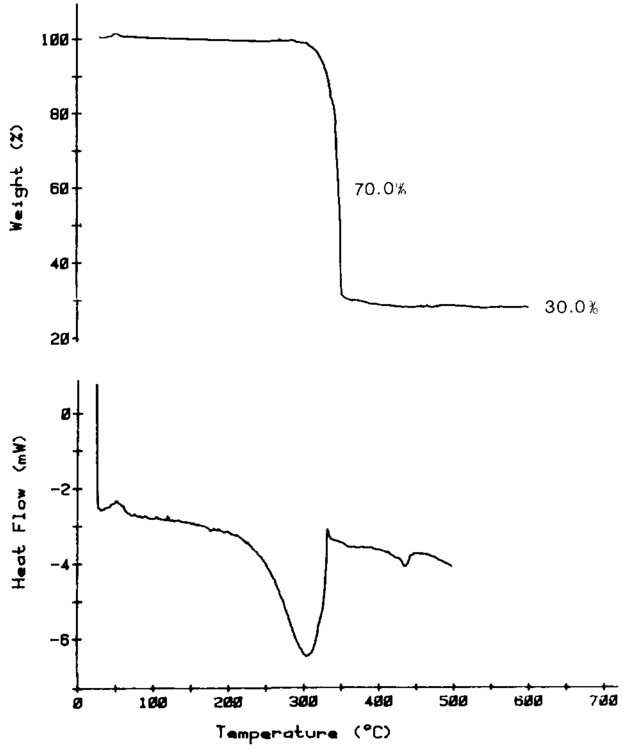

Fig. 7. Thermal analysis of $Zn(tnp)(NO_3)_2$.

for octahedral cobalt(II) complexes [23]. When the octahedral complex is trigonally distorted, the magnetic moment can be reduced from its maximum value by as much as 0.8 B.M. with only a 2% distortion [24]. A complex with a moment of 4.41 B.M. has been reported [25]; this complex has different ligands, including coordinated perchlorate ions, and would be expected to be distorted significantly from octahedral symmetry.

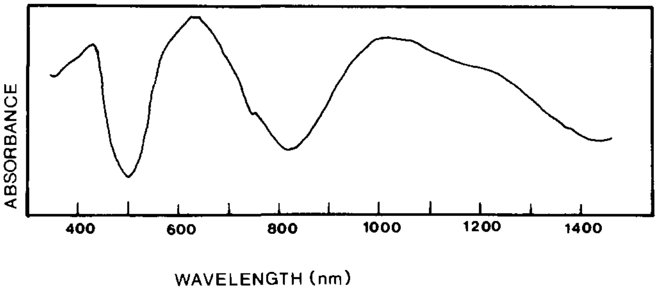

Fig. 8. Visible–near-infrared spectrum of $Ni(tnp)(NO_3)_2 \cdot H_2O$ at liquid nitrogen temperature.

The nitrate bands in the infrared are 1279 cm^{-1}, NO_2 symmetric stretch, 1014 and 1021 cm^{-1}, N–O stretch, and 805 cm^{-1}, nonplanar rock, which indicate coordinated nitrate. The combination bands at 1718 and 1776 cm^{-1} have a splitting of 58 cm^{-1} which is distinctive of bidentate bonding.

The thermogravimetric analysis shows a mass loss corresponding to 75.0%. This mass loss corresponds to the loss of the tnp ligand and the decomposition of the nitrate groups leaving either Co_3O_4 or CoO as the residue. For the formation of Co_3O_4, the calculated mass loss would be 74.45% and the cobalt content of the complex would be 16.6%. For the formation of CoO, the calculated mass loss would be 76.15% and the cobalt content of the complex would be 17.6%. From these data it is not possible to distinguish between these two possibilities. Between 515 and 535°C another mass loss occurs of 8.21% of the original sample. The nature of this decomposition is not known. Decompositions of Co_3O_4 into CoO + O_2 or of CoO into Co + O_2 have much smaller mass losses and are expected to occur only at much higher temperatures [26].

Based on the available evidence it appears that the cobalt complex has a tetragonal structure that is polymeric because the tnp ligands bridge between metal ions. The coordination sphere of the cobalt(II) also contains two bidentate nitrato groups. This results in a structure similar to that of the 1 : 1 copper complex previously reported [9] and shown in Fig. 2.

$Ni(tnp)(NO_3)_2 \cdot H_2O$

The nickel complex has one ligand per metal plus a molecule of water. The presence of water is confirmed by the mass loss in the TGA and by the presence of a broad absorption in the infrared spectrum near 3500 cm^{-1}. The thermal analysis shows an endothermic mass loss between 135 and 175°C which corresponds to the loss of one water molecule. This may be lattice water rather than water coordinated to the nickel since it is lost at a fairly low temperature. Coordinated water has a broad absorption in the infrared near 800 cm^{-1} for nickel(II) compounds. The ligand and the complex have sharp absorptions in this region and so it appears that the water is not coordinated to the nickel. The second decomposition near 340°C has a mass loss which corresponds to the loss of the ligand and the decomposition of the nitrate groups leaving NiO as the residue. The DSC shows exothermic peaks in the temperature range of this decomposition similar to those of the cobalt complex. The mass of the residue corresponds to 17.0% nickel in the original sample which agrees with the analytically determined value of 17.7%.

The nitrate bands in the infrared are 1005 and 1023 cm^{-1}, N–O stretch and 804 and 815 cm^{-1}, nonplanar rock, which indicate coordinated nitrate. The combination bands at 1720 and 1776 cm^{-1} have a splitting of 56 cm^{-1} which is distinctive of bidentate bonding.

TABLE 2

Experimental and calculated band positions (in cm^{-1}) for Ni(tnp)(NO$_3$)$_2$·H$_2$O

Transition	Calc.	Obs.	Transition	Calc.	Obs.
$^3B_{1g} \rightarrow {}^3B_{2g}$	8050	8050	$\rightarrow {}^1E_g$	21306	
$\rightarrow {}^3E_g$	9923	9920	$\rightarrow {}^1B_{2g}$	22054	
$\rightarrow {}^1A_{1g}$	13148	13250	$\rightarrow {}^1A_{1g}$	22955	
$\rightarrow {}^1B_{1g}$	13467		$\rightarrow {}^3E_g$	24142	23260
$\rightarrow {}^3E_g$	14835	16100	$\rightarrow {}^3A_{2g}$	24780	
$\rightarrow {}^3A_{2g}$	15400				

The magnetic moment of 3.18 B.M. is typical of octahedral nickel(II) complexes. The visible–near-infrared spectrum of the nickel complex at liquid nitrogen temperature is similar to that of a tetragonally distorted octahedral complex. If the structure of the complex is similar to that of Hatfield's copper complex shown in Fig. 2, the bidentate nitrate groups would be considered to be in the xy plane and the lowest energy absorption would equal $10Dq_{xy}$. The $^3A_{2g} \rightarrow {}^3T_{2g}(F)$ transition in O_h symmetry has been split into absorptions at 8050 and 9920 cm^{-1} which correspond to $^3B_{1g} \rightarrow {}^3B_{2g}$ and $^3B_{1g} \rightarrow {}^3E_g$ transitions in D_{4h} symmetry, respectively. If the assignments are correct, the following parameters, calculated as previously described [17], give a reasonable although not excellent fit to the spectrum: $Dq_{xy} = 805$ cm^{-1}, $Dt = -224$ cm^{-1}, $B = 750$ cm^{-1}, $Ds = -150$ cm^{-1}, $C = 3900$ cm^{-1}, and $Dq_z = 1200$ cm^{-1}. A comparison of the measured and calculated spectra is given in Table 2.

Cu(tnp)$_2$(NO$_3$)$_2$

The copper complex has two ligands per metal in contrast to the others which have only one. The complex is slightly soluble in toluene, 1,2-dichloroethane, acetone, ethanol, and methanol which indicates that it may not be polymeric. The magnetic moment of 1.73 B.M. is as expected for a copper(II) compound. The visible–near-infrared spectrum has a single absorption at 15600 cm^{-1} as is typical of copper(II) complexes.

The nitrate bands in the infrared are 1274 cm^{-1}, NO$_2$ symmetric stretch, 1017 cm^{-1}, N–O stretch, and 806 cm^{-1}, nonplanar rock, which indicate coordinated nitrate. The combination bands at 1719 and 1760 cm^{-1} have a splitting of 41 cm^{-1} which is distinctive of bidentate bonding. In general, the infrared spectrum is nearly identical to that reported for the 1 : 1 complex [9].

The thermogravimetric analysis shows two decompositions. The first between 160 and 215°C corresponds to the loss of one tnp ligand. This leaves Cu(tnp)(NO$_3$)$_2$ as the residue, which is the compound studied by Hatfield and co-workers [9]. The second decomposition between 250 and

340°C corresponds to the loss of the second ligand and the decomposition of the nitrate groups leaving CuO as the residue. The 17.6% residue corresponds to 14.1% copper in the original sample which agrees well with the analytically determined value of 14.1%.

The structure of this 2 : 1 ligand-to-metal complex must be different from the structure of the 1 : 1 complexes. Two bidentate nitrate groups would occupy four bonding sites on the copper(II) ion. Thus the two tnp ligands must occupy only two bonding sites if the copper(II) ion is to be six coordinate. This would suggest that this complex is not polymeric but consists of discrete $[Cu(tnp)_2(NO_3)_2]$ units. If so, this compound should be more soluble in nondestructive solvents and, indeed, it is slightly soluble in solvents such as toluene, acetone, methanol, and 1,2-dichloroethane.

$Zn(tnp)(NO_3)_2$

The thermogravimetric analysis of the zinc complex shows a single mass loss between 325 and 360°C which corresponds to the loss of the tnp ligand and the decomposition of the nitrate groups. The DSC in this temperature range appears different from the others. It is largely endothermic whereas the others are largely exothermic. The decompositions seem to have at least two and maybe three components with the relative magnitudes of the components differing from compound to compound. For the cobalt, nickel, and copper complexes, the first component is endothermic and is small; the subsequent components are strongly exothermic. For the zinc complex, the first endotherm is large. This difference for zinc may indicate a different mechanism of decomposition for the zinc complex compared to the other three which seem to have the same decomposition mechanism. A series of compounds in which the decomposition of the zinc compound appeared to be different has previously been reported [27].

The nitrate bands in the infrared are 1292 cm^{-1}, symmetrical stretch, 1019 cm^{-1}, N–O stretch, and 812 cm^{-1}, nonplanar rock, which indicate coordinated nitrate. The combination bands at 1720 and 1775 cm^{-1} have a splitting of 55 cm^{-1} which is distinctive of bidentate bonding.

CONCLUSIONS

In all the complexes reported, the nitrate ions function as bidentate ligands. The complexes with a ligand-to-metal ratio of 1 : 1 are polymeric with bridging ligands in a manner proposed previously [9]. The copper(II) complex has a ligand-to-metal ratio of 2 : 1 and, although containing bidentate nitrate groups, appears to be monomeric with monodentate ligands.

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