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Metal Complexes of Pyridine-3-Carboxyaldehyde Thiosemicarbazone

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Complexes of copper(II), cobalt(II), nickel(II), manganese(II), iron(II) and iron(III), zinc(II) and silver(I) with pyidine-3-carboxaldehyde thiosemicarbazone (HNAT) are reported. Analytical, spectral, magnetic and conductance studies indicate that HNAT acts as a bidentate ligand in all its complexes coordinating through the nitrogen of the pyridine ring and sulphur atom. Polymeric six-coor-dinated ligand bridged structures have been proposed for all the complexes except [Co(HNAT)Cl$_2$], which has a polymeric four-coordinated structure.

INTRODUCTION

In continuation of our studies on the transition metal complexes of biologically active thiosemicarbazones[1, 2], we now report the metal complexes of pyridine-3-carboxaldehyde thiosemicarbazone (HNAT)(I). Literature records only one report on the existence of mercury(I) and (II), copper(II) and palladium(II) complexes of HNAT[3].

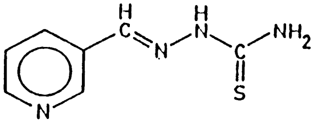

Fig. 1

EXPERIMENTAL

HNAT was obtained commercially from Fluka AG, Chemische Fabrik, CH-9470 Buchs S.G. Anhydrous ferric chloride was obtained commerially from Sarabhai Chemicals. Iron(II) chloride was obtained by reducing iron(III) chloride with chlorobenzene. Other anhydrous metal chlorides were prepared by methods reported in literature. Solutions of Co(NCS)$_2$, NiI$_2$ and Ni(ClO$_4$)$_2$ were obtained by reacting the appropriate metal chloride (0.01 m) with potassium thiocyanate/iodide/perchlorate (0.02 M) in absolute alcohol, chilling the resulting solution and filtering off the potassium chloride.

The complexes were prepared by refluxing the respective metal salt solution (0.01 M) with HNAT (0.02 M) in ethanol for 0.5 h when solid complexes separated out. The iron(II) complex was prepared in a nitrogen atmosphere and it separated out immediately on mixing anhydrous iron(III) chloride and HNAT

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(1 : 2) in absolute ethanol. The iron(III) chloride complex separated out on stirring the reaction mixture for 2 h.

Infrared spectra were recorded on a 'Perkin-Elmer 631' infrared spectrophotometer in the 4000–200 cm^{-1} region as nujol and hexachlorobutadiene mulls or as KBr pellets. Electronic spectra were taken in appropriate solvents and scanned over 50.0–12.5 kK region in one cm matched quartz cells on 'Specord UV Visible' spectrophotometer. Diffuse reflectance spectra of the powdered samples were recorded on a Unicam SP 700A UV and visible spectrophotometer over 33.3 to 5.0 kK region. The ESR spectrum of the copper(II) complex was recorded at room temperature as the first derivative of the absorption signal using Jeol, JES-FE 3X spectrometer. The magnetic susceptibility of the complexes was determined by Gouy's method at room temperature using mercury tetrathiocyanatocobaltate(II) as a standard. The conductivity measurements were carried out on Toshniwal Cl-01-02A type conductivity bridge for freshly prepared 10^{-3} M solutions at 25°C.

Microanalysis for the elements carbon, hydrogen and nitrogen was carried out in the Microanalytical Laboratory of the Chemistry Department, Panjab University, Chandigarh. Metal contents of the complexes were determined by standard methods.

RESULTS AND DISCUSSION

The complexes isolated during the present investigations are listed in Table-1 along with their structural formulae, colour and analytical data.

The infrared spectrum of HNAT shows three bands at 3395, 3320 and 3240 cm^{-1} in the NH stretching region. These bands occur in the same region or are shifted to higher frequencies in the complexes showing that NH_2 is not participating in coordination[4]. The medium intensity band at 1615 cm^{-1} in the spectrum of HNAT has been assigned to a combination of the NH_2 deformation and (C═N) stretching vibrations. This band remains almost unshifted in the complexes indicating that nitrogen of the azomethine group is not coordinating[2].

Coordination of sulphur atom in HNAT to the metal atom should result in the lowering of (C═S) bond order with consequent decrease in ν(CS), the (C—N) bond order, on the other hand, should increase.[5] The bands appearing in the HNAT spectrum at 1355, 1270, 1085, 1070 and 815 cm^{-1} have been assigned to combinations of ν(CS), ν(CN) and $\delta(NH_2)$ modes. The former two have smaller contribution but the latter three have large contribution from the CS stretching mode, with the band at 815 cm^{-1} being almost pure ν(CS) vibration. The strong band at 1085 cm^{-1} and the medium strong intensity band at 1070 cm^{-1} are either absent in the spectra of the complexes or are present with much reduced intensity. The 815 cm^{-1} band which is sandwiched between two CH deformation bands of the pyridine ring at 825 and 795 cm^{-1} moves to lower frequency 805–800 cm^{-1}. These observations suggest that the sulphur atom is coordinating to the metal ions in all the complexes.

In HNAT itself the =C⩦C and =C⩦N stretching vibrations of the pyridine ring appear at 1592, 1580, 1460, 1410 cm^{-1}, the ring breathing at 1040 cm^{-1} and the in-plane and out-of-plane deformations of the pyridine ring at 615 and 410

TABLE-1
ANALYTICAL DATA AND COLOUR OF THE COMPLEXES

Complex/Colour	Analytical Data, Found (Calcd.) %					
	Metal	Halogen	Sulphur	Carbon	Hydrogen	Nitrogen
$[Cu_2(HNAT)_3Cl_2]$	15.43	17.54	11.99	31.89	2.98	19.81
Yellowish green	(15.70)	(17.55)	(11.87)	(31.15)	(2.96)	(20.76)
$[Cu_2(HNAT)Cl_2]$	18.97	22.62	10.66	27.44	3.45	18.95
Blue	(19.01)	(22.99)	(10.32)	(27.10)	(3.25)	(18.06)
$[Co(HNAT)_2(NCS)_2]\cdot C_2H_5OH$	9.90	—	21.52	37.04	3.95	24.02
Pale pink	(10.14)		(21.95)	(37.18)	(3.78)	(24.05)
$[Ni(HNAT)_2Cl_2]$	11.75	14.79	13.21	33.45	4.50	22.57
Yellowish green	(11.99)	(14.50)	(13.07)	(34.31)	(3.26)	(22.88)
$[Ni(HNAT)_2I_2]$	7.94	33.24	8.89	27.14	3.69	14.63
Yellowish green	(7.68)	(33.21)	(8.37)	(28.26)	(3.66)	(14.64)
$[Ni(HNAT)_2(H_2O)_2(ClO_4)_2]$	8.89	10.88	9.72	26.70	4.40	17.86
Green	(8.98)	(10.86)	(9.79)	(25.69)	(3.06)	(17.13)
$[Ni(HNAT)_2(H_2O)_2(NO_3)_2]$	9.93	—	10.92	28.80	3.44	24.00
Pale green	(10.14)		(11.08)	(28.03)	(3.46)	(24.99)
$[Mn(HNAT)_2Cl_2]$	11.28	14.60	13.32	35.27	2.40	22.36
White	(11.32)	(14.61)	(13.17)	(34.54)	(3.30)	(23.04)
$[Mn(HNAT)_2Br_2]$	9.17	25.70	10.52	27.42	3.58	18.61
Pale yellow	(9.00)	(26.19)	(10.48)	(27.51)	(3.27)	(18.32)
$[Fe(HNAT)_2Cl_2]$	11.39	14.42	12.94	34.47	3.39	22.93
Light yellow	(11.48)	(14.59)	(13.15)	(34.51)	(3.29)	(23.01)
$[Fe(HNAT)_2Cl_2]Cl$	10.77	20.70	12.70	32.54	3.10	21.69
Yellow	(10.69)	(20.39)	(12.26)	(32.20)	(3.06)	(21.39)
$[Zn(HNAT)_2Cl_2]$	13.07	14.26	13.04	34.25	3.22	22.27
Pale yellow	(13.17)	(14.62)	(12.89)	(33.85)	(4.10)	(22.56)
$[Ag(HNAT)_2]NO_3$	20.50	—	12.12	39.53	3.60	22.30
Pale yellow	(20.37)		(12.08)	(31.71)	(3.02)	(22.56)

cm^{-1} respectively. In the spectra of all the complexes these bands either shift to higher frequencies or remain almost unchanged as compared to their positions in the ligand. This can be considered as sufficient proof that the pyridinic nitrogen is coordinating in all the complexes[6].

The above interpretation of the spectra of HNAT and its complexes, therefore, favours a bidentate character of the ligand in all its complexes with the pyridinic nitrogen and the sulphur atom acting as the donor atoms. A skeletal molecular model of HNAT shows that the two donor atoms are at such a distance from one another that it will not be possible for both of them to coordinate to the same metal ion. The complexes will, therefore, be either dimeric or polymeric with each metal ion having 4, 5 or 6 coordination.

Copper(II) forms a greenish yellow complex $CuCl_2\cdot 1.5HNAT$ with a metal to ligand ratio of 2 : 3. Since HNAT is bidentate all probable 6, 5 or 4 coordinated structures must be polymeric with ligand bridges. The fact that the complex is insoluble in all common organic solvents (except dimethylformamide) also supports its polymeric nature. The solid state spectrum of the complex shows two bands at 14.8 and 24.4 kK. The number and position of these spectral bands is similar to those present in polymeric octahedral complexes of copper(II) with thiosemicarbazide[7] and Schiff bases[8]. The electronic spectrum of the complex in DMF shows only one absorption band at 26.6 kK which indicates that the species present in solution are different from those in the solid state. Hence the measured molar conductance in DMF ($\Lambda_M = 77.8$ ohm^{-1} cm^{-2} mole^{-1}) is not very meaningful. The magnetic moments of magnetically dilute copper(II) complexes are generally in the range 1.75–2.20 B.M. at room temperature, regardless of stereochemistry. However, the magnetic moment of the complex under discussion has been found to be 1.47 B.M. The low magnetic moment suggests that there is a weak antiferromagnetic coupling of the unpaired electrons on the adjacent copper(II) ions, either through a direct metal-metal interaction or through the agency of the orbitals of the bridging chlorine atoms. The ESR spectrum of the powdered sample at room temperature suggested that it is an isotropic spectrum with $g_{iso} = 2.16$. Such a spectrum in this complex might be due to the complex containing a grossly misaligned "tetragonal" axis[9]. The spectrum is similar to the spectra of dimeric/polymeric compounds[10] which show distinct δ m = 2 transition in the region g *ca.* 4 and H_0 *ca.* 1500 G. In the complex under study this transition is observed at g *ca.* 4.62 and H_0 *ca.* 1460 G. The spin states of this transition are degenerate in the absence of magnetic field and ESR spectrum in this region is, to a first order, independent of the zero-field splitting. This transition has a low probability, being spin forbidden. A structure which will justify all the properties exhibited by the complex will be the one in which chlorine bridged dinuclear units are joined by long ligand bridges to give a polymeric structure. One of the two copper atoms in the units is surrounded by 3 chlorine, 2 nitrogen and 1 sulphur atoms and the other by 3 chlorine, 1 nitrogen and two sulphur atoms (Fig. 2). The arrangement of donor atoms around each copper atom is distorted octahedral. The proximity of two copper atoms to each other in the dinuclear unit will account for the low magnetic moment and the ESR of the complex.

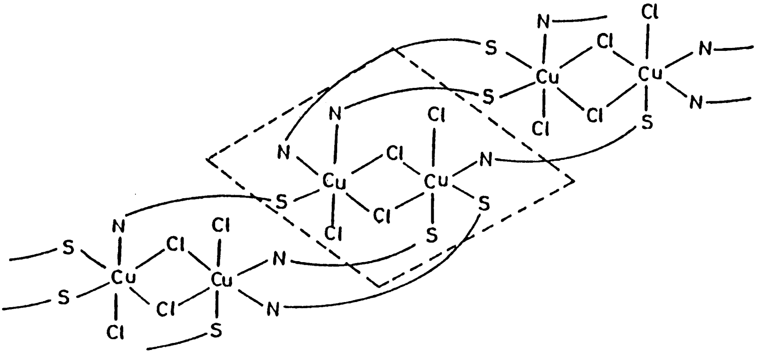

Fig. 2

Cobalt(II) chloride and cobalt(II) thiocyanate form complexes of empirical formula $CoCl_2 \cdot HNAT$and $Co(NCS)_2 \cdot 2HNAT \cdot C_2H_5OH$ respectively. The blue coloured complex $CoCl_2 \cdot HNAT$ is insoluble in most organic solvents and is nonionic in dimethylformamide (Λ_M = 3.23 ohm^{-1} cm^2 $mole^{-1}$). The magnetic moment of the complex has been found to be 4.21 BM at room temperature which suggests a tetrahedral stereochemistry. Its electronic spectrum is dominated by high energy absorption band centred around 16 kK which appears to be split into three closely spaced bands at 14.92, 15.87 and 16.94 kK. In the near infrared region there are two closely spaced strong bands at 5.9 and 7.8 kK which also appear to be the split components of a strong band centred around 7 kK. Since cobalt(II) tetrahedral complexes are known to show a strong band in the visible region (14–16 kK) and another one in the infrared region (5–9 kK), these two sets of bands may be considered as corresponding to the $^4T_1(F) \leftarrow {}^4A_2$ and $^4T_1(P) \leftarrow {}^4A_2$ transitions respectively of cobalt(II) in a tetrahedral symmetry[11]. The solution spectrum of the complex in DMF in the visible region also exhibits a strong band with split components at 14.75 and 16.5 kK not far removed from their position in the solid state spectrum. In view of the above observation a ligand bridged dimeric or polymeric (Fig. 3) structure in which the cobalt ions are surrounded by two chlorine, one sulphur and one nitrogen atom in distorted tetrahedral arrangement is suggested for the complex. Structures of these types have been proposed for dichloro(methylpyrazine) cobalt(II) complexes by Lever *et al*[11].

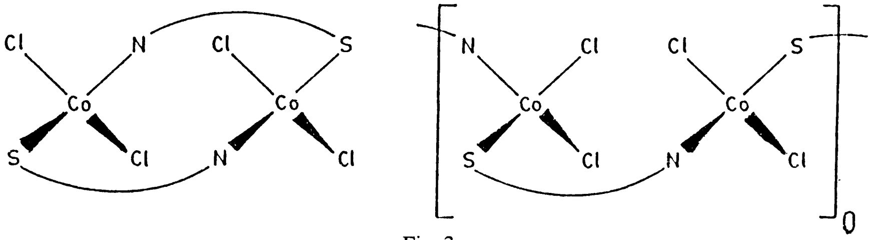

Fig. 3

The pink cobalt(II) complex, $Co(NCS)_2 \cdot 2HNAT \cdot C_2H_5OH$ is essentially a nonelectrolyte in methanol though it shows appreciable conductance due to solvolysis (Λ_M = 33.42 ohm^{-1} cm^2 $mole^{-1}$). The infrared spectrum of the complex exhibits three bands at 2085, 822 and 490 cm^{-1} which might be attributed to the C═N and C—S stretching and N═C═S bending vibration of N-bonded terminal thiocyanato group[12]. The magnetic moment of the complex is 4.9 B.M. which is diagnostic of a spin-free cobalt(II) octahedral species. In the solid state spectrum of the complex two absorption bands are observed at 18.07 (ν_3) and 8.50 (ν_1) kK attributed to octahedral symmetry. No band due to ν_2 transition is observed, probably due to the weakness of the band and its proximity to the ν_3 transition. The solution of the complex in methanol shows a band at 20 kK which is shifted from its position in the solid state spectrum, probably due to the slight interaction between the solute and the solvent. This accounts for the appreciable conductance shown by the complex. The solution of the complex in dimethylformamide is blue and shows a strong band at 15.8 kK with a shoulder at 17.0 kK typical of cobalt(II) in a tetrahedral environment indicating that the complex decomposes in DMF. On the basis of the above evidence the complex $[Co(HNAT)_2(NCS)_2]\cdot C_2H_5OH$ can be assigned a polymeric six-coordinated ligand bridged structure in which each cobalt atom is surrounded by two nitrogen and two sulphur atoms of HNAT in the equatorial plane and the axial positions are occupied by the nitrogen atom of the thiocyanato groups.

Of the four nickel(II) complexes synthesised, $NiCl_2\cdot 2HNAT$ ($\Lambda_M = 2.90$ ohm^{-1} cm^2 mole^{-1} in dimethyl formamide) and $NiI_2\cdot 2HNAT\cdot C_2H_5OH$ ($\Lambda_M =$ 43.34 ohm^{-1} cm^2 mole^{-1} in ethanol) are non-electrolytes while $Ni(NO_3)_2 \cdot 2HNAT\cdot 2H_2O$ ($\Lambda_M = 130.0$ ohm^{-1} cm^2 mole^{-1} in DMF) and $Ni(ClO_4)_2\cdot 2HNAT \cdot 2H_2O$ ($\Lambda_M = 2650.0$ ohm^{-1} cm^2 mole^{-1} in water) are 1 : 2 electrolytes. The ionic nature of the latter two complexes is also supported by their infrared spectra. The nitrate complex shows a medium intensity band at 1405 cm^{-1} and a strong band at 825 cm^{-1} due to ionic nitrate[13] and the perchlorate complex displays only one broad band between 1150 and 1070 cm^{-1} attributed to the ν_3 transition of ionic perchlorates[14]. A weak band at 3460 cm^{-1} and shoulder at 1630 cm^{-1} in the two complexes can be attributed to OH stretching and to the HOH bending mode of the water molecules respectively. The room temperature magnetic moments of all the four complexes are between 3.01–3.29 B.M., which is well within the expected range of the divalent nickel ion in an octahedral field.

The solid state electronic spectra of the four complexes show three bands in the region 23.2 to 8.6 kK (the chloro complex at 22.22, 14.40 and 8.58 kK; the iodo complex at 23.26, 14.92 and 9.26 kK; the nitrate complex at 21.74, 14.70 and 9.52 kK and the perchlorate complex at 22.00, 14.70 and 9.43 kK) which may be assigned to the spin-allowed transition $^3T_{1g}(P) \leftarrow {}^3A_{2g}(\nu_3)$, $^3T_{1g}(F) \leftarrow {}^3A_{2g}(\nu_3)$ and $^3T_{2g} \leftarrow {}^3A_{2g}(\nu_1)$ typical of six coordinated complexes[15]. That the distortion from regular octahedral environments around nickel atom is small, is indicated by non-splitting of the ν_2 and ν_3 bands. Moreover the ν_2/ν_1 ratio for all the complexes is within the range 1.5–1.7 reported for octahedral nickel(II) complexes. The solution spectra of the complexes show only the ν_3 band which is slightly shifted from its position in the solid state spectrum in most of the complexes.

Manganese(II) chloride and bromide react with HNAT to give an almost white complex of composition $MnCl_2\cdot 2HNAT$ and a pale yellow complex of composition $MnBr_2\cdot 2HNAT\cdot 2H_2O$. The former complex is a non-electrolyte in methanol, though it shows some conductance due to solvolysis ($\Lambda_M = 37.4$ ohm^{-1} cm^2 mole^{-1}). The manganese(II) bromide complex reacts readily with most of the solvents used for the determination of molar conductance and the conductance values in different solvents are at variance with one another. The observed room temperature magnetic moments of the two complexes are 5.5 and 5.8 B.M. respectively. Both the complexes are thus high spin. The solid state spectrum of each of the two complexes shows only one weak absorption peak at 17.7 kK in the visible region. This band can be assigned to the $^4T_{1g}(G) \leftarrow {}^6A_{1g}$ transition in an octahedral field[16].

Iron(II) chloride forms a yellow coloured complex, $FeCl_2\cdot 2HNAT$, with HNAT. The complex is nonionic in nature ($\Lambda_M = 26.5$ ohm^{-1} cm^2 mole^{-1}) in dimethylformamide). The magnetic moment of the complex, 4.98 B.M., is somewhat less than

TABLE-2
SPECTRAL BANDS MOLAR CONDUCTANCE AND MAGNETIC MOMENT OF THE COMPLEXES OF HNAT

Complex	Position of absorption bands (kK)	Molar conductance ohm^{-1} cm^2 mol^{-1}	Magnetic moment of metal atom at room temp. (B.M.)
$[Co(HNAT)Cl_2]$	A. 14.92, 15.83, 16.94, 7.8, 5.9 B. 14.75 ($E = 2.5 \times 10^3$)	3.23*	4.21
$[Co(HNAT)_2(NCS)_2]\cdot C_2H_5OH$	A. 18.7, 8.5 B. 20.0 ($E = 47.86$)	33.42†	4.97
$[Ni(HNAT)_2Cl_2]$	A. 22.22, 14.4, 8.58 B. 23.2 ($E = 58.6$)	2.90*	3.01
$[Ni(HNAT)_2I_2]\cdot 2C_2H_5OH$	A. 23.26, 14.92, 9.26 B. 22.0 ($E = 17.3$)	43.34‡	3.29
$[Ni(HNAT)_2(H_2O)_2](NO_3)_2$	A. 21.74, 14.7, 9.52 B. 22.0 ($E = 34.55$)	130.0*	3.16
$[Ni(HNAT)_2(H_2O)_2](ClO_4)_2$	A. 22.0, 14.7, 9.43 B. 22.0 ($E = 45.55$)	265.0**	3.17
$[Mn(HNAT)_2Cl_2]$	A. 17.7	374†	5.50
$[Mn(HNAT)_2Br_2]\cdot 2H_2O$	A. 17.7	—	5.81
$[Fe(HNAT)_2Cl_2]$	A. 24.0, 10.0, 6.22	26.5*	4.98
$[Fe(HNAT)_2Cl_2]Cl$	A. 25.0, 20.0 B. 25.0 ($E = 6.32 \times 10^3$) . 20.0 ($E = 2.36 \times 10^3$)	135.2*	5.73
$[Zn(HNAT)_2Cl_2]$	—	4.7††	—
$[Ag(HNAT)_2](NO_3)$	—	32.3††	—

A.Solid B. Solution *DMF †Methanol ‡Ethanol **Water ††DMSO

the value expected for high spin octahedral complexes, probably due to deviation from pure octahedral symmetry. The solid state spectrum of the complex shows absorption bands at 24.0, 10.0 and 6.2 kK. The highly intense band at 24 kK is due to the charge transfer transition and is responsible for the yellow colour of the complex. The other two bands can be assigned to the transition from the $^5T_{2g}$ ground state to the split components of the ^5E_g state in the distorted octahedral field[17].

The orange yellow complex of iron(III), $FeCl_3\cdot 2HNAT$,is a 1 : 1 electrolyte in dimethylformamide ($\Lambda_M = 135.2$ ohm^{-1} cm^2 mole^{-1}). The magnetic moment of the complex is 5.73 B.M. which is a little lower than the expected value of 5.9 B.M. for spin-free iron(III) in an octahedral field. The electronic spectrum of the complex, both in the solid state and in DMF solutions, shows a very strong and broad band at 25 kK with a shoulder at 20 kK. This is most probably a charge transfer band and is responsible for the colour of the complex. The d-d transitions are apparently obscured by the strong charge transfer band[15].

HNAT forms a pale yellow complex of the composition $ZnCl_2 \cdot 2HNAT$ which is a non-electrolyte in DMF (Λ_M = 4·7 ohm^{-1} cm^2 $mole^{-1}$). Silver(I) nitrate forms a yellowish white complex, $AgNO_3 \cdot 2HNAT$. The molar conductance of the complex in dimethylsulfoxide shows that the complex is a 1 : 1 electrolyte (Λ_M = 32.3 ohm^{-1} cm^2 $mole^{-1}$). The ionic nature of the nitrate is also supported by the infrared spectrum of the complex which shows a broad band at 1360–1280 cm^{-1} and a strong band at 810 cm^{-1}.

All the complexes (except $CoCl_2 \cdot HNAT$ and $AgNO_3 \cdot 2HNAT$ which are four-coordinate) isolated are six-coordinate with HNAT acting as a bidentate ligand coordinating through the pyridine nitrogen and the sulphur atom and structures similar to that of $[Co(HNAT)_2(NCS)_2] \cdot C_2H_5OH$. The observation that pyridine-3-carboxaldehyde thiosemicarbazone (HNAT) behaves as a neutral bidentate ligand is at variance with the coordination behaviour of pyridine-2-carboxaldehyde thiosemicarbazone (HPAT) which shows three types of coordination behaviour. The latter can act as unidentate, bidentate or tridentate ligand and might be either neutral or monobasic in its complexes[2]. With metals which show variable valency, HPAT stabilises the higher oxidation state of the metal thus oxidising cobalt(II) to cobalt(III) in the presence of air. In contrast, HNAT acts only as a bidentate bridging ligand forming polymeric complexes. It does not oxidise cobalt(II) to cobalt(III) even on passing air through the reaction mixture.

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