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Chelating Properties of A New Pyrazole-based ONS Tridentate Ligand: Cobalt(II) & Nickel(II) Complexes with 5-Methyl-1-thiocarbamyl-pyrazole-3-carboxylic Acid

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With 5-methyl-1-thiocarbamylpyrazole-3-carboxylic acid ($TMPCH_2$) as the primary ligand, mixed complexes of the types M(TMPC)B.nH_2O [M=Co, B=H_2O/py/pico (α-, β- & γ-)/bipy/*o*-phen, n = 1 or 5; M = Ni, B=NH_3/α-pico/bipy/*o*-phen, n = 1] and Ni (TMPC). 3B[B=py/β-pico/γ-pico] have been isolated and characterised. Magnetic moment and electronic spectral data indicate that majority of the nickel(II) complexes and the bipyridyl and *o*-phenanthroline adduct of cobalt(II) are octahedral in nature while the cobalt(II) complexes with water or monodentate heterocyclic base molecules as coligands are composed of both tetrahedral and octahedral varieties. The ammonia adduct of nickel(II) appears to be a mixture of paramagnetic octahedral and diamagnetic square-planar forms. IR data suggest diprotic (ONS) tridentate function of the primary ligand in its thiol form in all these mixed-ligand species.

A NUMBER of thiosemicarbazones containing nitrogen heterocycles are well known for their carcinostatic activity[1], which, by loss of protons from their tautomeric thiol forms, can act as potential tridentate ligands sequestering metal ions involved in carcinogenesis. As a part of our programme[2] on the investigation of coordination properties of pyrazole-based ligands, the present paper reports the synthesis and chelating properties of 5-methyl-1-thiocarbamylpyrazole-3-carboxylic acid [abbreviated as $TMPCH_2$; I(a, b)] having ONS donor set. Solid mixed ligand complexes of the types M(TMPC) B.nH_2O [M = Co, B = H_2O/py/pico (α-, β- & γ-)/bipy/*o*-phen, n = 1 or 5; M = Ni(B = NH_3/α-pico/bipy/*o*-phen, n = 1] and Ni(TMPC). 3B[where B= py/β-pico/γ-pico] have been characterised on the basis of elemental analyses and various physicochemical techniques.

Materials and Methods

5-Methyl-1-thiocarbamylpyrazole-3-carboxylic acid ($TMPCH_2$) was prepared by condensation reaction between sodium salt of ethyl acetopyruvate and thiosemicarbazide hydrochloride following the method of Knorr *et al.*[3] The product recrystallised from ethanol as pale yellow microcrystalline solid m.p. 204-6° (d) (Found : C, 39.53; H, 3.92; N, 22.55%. $C_6H_7N_3O_2S$ requires C, 38.91; H, 3.86; N, 22.69%; λ_{max}^{MeOH} 212 nm (log ε ~3.92), 239 nm (log ε ~3.91), 289 nm (log ε ~3.99).

Preparation of the complexes: *Co (TMPC).2H_2O* — Aqueous alcoholic solutions of cobalt(II) acetate tetrahydrate (0.01 mol) and $TMPCH_2$ (0.01 mol) were mixed, dilute ammonia was added to bring the *p*H around 5. This was kept in a dessicator over conc. H_2SO_4 for 24 hr when a dirty pink coloured compound separated out.

Co(TMPC)B.H_2O, where B = py/pico (α-, β- & γ-) — To the resulting solution obtained by mixing aqueous alcoholic solutions of cobalt chloride hexahydrate (0.01 mol) and the primary ligand (0.01 mol) was added the respective base (pyridine or picoline) dropwise till a change of colour (pink to deep red; *p*H≈5) was noticed. On keeping for 48 hr at room temperature, the desired mixed ligand complexes separated out.

Ni(TMPC)NH_3.H_2O — The *p*H of the resulting solution obtained by mixing aqueous ethanolic solutions of $NiCl_2.6H_2O$ (0.01 mol) and the ligand (0.01 mol) was adjusted to around 7 by dilute ammonia. Red compound separated out within 30 min.

Ni(TMPC).3B, where B=py/β-pico/γ-pico — These compounds were isolated by two different routes :

(i) The red Ni(TMPC)$NH_3.H_2O$ (0.002mol) on dissolution in 20-25 ml of the respective base produced blue solution which on keeping in air for about 48 hr gave the desired base adduct.

(ii) The *p*H of the solution obtained by mixing aqueous ethanolic solutions of $NiCl_2.6H_2O$(0.01mol) and the ligand (0.01 mol) was adjusted around 6 by the dropwise addition of the respective base; the corresponding base adduct separated as shining blue crystals within 48 hr. This method was successful in isolating the olive-green Ni(TMPC) α-pico. H_2O.

M(TMPC).B.H_2O, where B = bipy/o-phen; M = Co/Ni, n = 1 or 5 — Aqueous ethanolic solutions of $MCl_2.6H_2O$ (0.01 mol), ligand (0.01 mol) and of bipyridyl or *o*-phenanthroline (0.01 mol) were mixed together; the *p*H of the resulting solution was adjusted to around 6 by the dropwise addition of dilute ammonia when a coloured microcrystalline compound separated out within 30 minutes.

TABLE 1 — ANALYTICAL AND MAGNETIC MOMENT DATA OF THE MIXED-LIGAND COMPLEXES OF Co(II) AND Ni(II)

Complex (μ_{eff} B.M.)*	Colour	Found (%) (calc.)*				
		Co/Ni	C	H	N	S†
Co(TMPC)2H_2O (4.25)	Dirty pink	21.20 (21.22)*	24.93 (25.90)	2.92 (3.24)	15.14 (15.11)	11.67 (11.51)
Co(TMPC)py.H_2O (4.60)	Do	17.43 (17.41)	38.27 (38.95)	3.10 (3.54)	16.44 (16.52)	9.53 (9.44)
Co(TMPC)α-pico. H_2O (4.69)	Grey pink	16.69 (16.71)	—	—	15.90 (15.86)	9.13 (9.06)
Co(TMPC)β-pico. H_2O (4.63)	Light pink	16.76 (16.71)	—	—	15.77 (15.86)	9.02 (9.06)
Co(TMPC)γ-pico.H_2O (4.73)	Do	16.74 (16.71)	41.79 (40.82)	4.16 (3.97)	15.85 (15.86)	9.09 (9.06)
Co(TMPC)bipy.H_2O (4.41)	Orange pink	14.18 (14.19)	—	—	16.87 (16.83)	7.73 (7.69)
Co(TMPC)*o*-phen.5H_2O (4.56)	Yellowish pink	11.56 (11.53)	41.00 (42.20)	4.30 (4.49)	13.67 (13 68)	6.18 (6.25)
Ni(TMPC)NH_3H_2O (2.18)	Red	21.18 (21.21)	25.08 (26.02)	3.76 (3.61)	20.29 (20.24)	11.44 (11.56)
Ni(TMPC).3py (2.98)	Blue	12.30 (12.27)	52.09 (52.65)	4.00 (4.18)	17.50 (17.55)	6.79 (6.69)
Ni(TMPC)α-pico.H_2O (3.11)	Olive green	16.62 (16.63)	40.12 (40.83)	4.18 (3.97)	15.90 (15.86)	9.10 (9.06)
Ni(TMPC)3β-pico (3.09)	Pale blue	11.30 (11.27)	—	—	16.09 (16.14)	6.10 (6.15)
Ni(TMPC)3γ-pico (3.14)	Do	11.20 (11.27)	—	—	16.21 (16.14)	6.08 (6.15)
Ni(TMPC)bipy.H_2O (2.96)	Blue	14.15 (14.12)	46.00 (46.19)	2.70 (2.87)	16.74 (16.85)	7.63 (7.70)
Ni(TMPC)*o*-phen. H_2O (2.87)	Blue violet	13.38 (13.34)	—	—	15.90 (15.91)	7.16 (7.27)

*At 303K, †Estimated gravimetrically as $BaSO_4$.

Physical measurements — Elemental analyses, magnetic susceptibility, electronic and vibrational spectral measurements were carried out as described earlier[4], unless otherwise stated. Thermal analyses were done in an open-air thermobalance of local design upto 600° with a heating rate of 7°C/minute.

Results and Discussion

The analytical data of the mixed ligand complexes and the magnetic moment values are compiled in Table 1. All the compounds are either insoluble or very little soluble in water and common organic solvents. They are, however, appreciably soluble in coordinating solvents like DMF, pyridine, picolines etc.

Cobalt(II) complexes — The magnetic moment values (4.25-4.73 B. M. at 303 K) of the mixed cobalt (II) complexes are, in general, low in comparison to the values prescribed for the normal 6-coordinate pseudo-octahedral species. On the basis of the magnetic moment data either a tetrahedral geometry or an octahedral one with lower symmetry can be suggested for these complexes. The diffuse reflectance spectral measurements† (upto 5000) reveal the following characteristic features :

(i) The prominent lowest energy broad band appearing at 8696 in the case of Co(TMPC)B.H_2O [B = H_2O/py/pico (α-, β- & γ-)] and at 10,000 in the case of Co(TMPC)B.nH_2O [B = bipy/*o*-phen] is assigned to the transition $^4T_{1g}$ $(F) \rightarrow {}^4T_{2g}(F)$ (ν_1) in an overall O_h symmetry. The weaker bands (with low intensity) at 7,000 and 6,000 might arise due to ligand over-tone modes.

(ii) The multiple split band around 20,000-20,500 is tentatively ascribed to transition $^4T_{1g}(F) \rightarrow {}^4T_{1g}$ (P) (ν_3) in an average O_h symmetry.

For the species, Co(TMPC)B.H_2O[B = H_2O/py/picolines] an additional high intensity pectral band at ~16,000 cm^{-1} accompanied by a split component at ~17,000 can reasonably be attributed to the transition $^4A_2 \rightarrow {}^4T_1$ (P) (ν_3) in a tetrahedral field[5] and logically these mixed species can be thought of as resulting from the coexistence of both tetrahedral and octahedral varieties[6]; the four-coordinate cobalt(II) species Co(TMPC)B.H_2O seem to be primarily tetrahedral in nature. These through extensive molecular association via the secondary coordination sites of $TMPCH_2$ might give rise to octahedral species within the same compound.

The mixed chelates containing bidentate heterocyclic amines are thought to be polymeric octahedral ones.

Nickel(II) complexes — The magnetic moment values (2.83-3.4 B.M. at 303K) of these mixed nickel(II) complexes are in the range expected for six-coordinate spin free pseudo-octahedral species.

The *F*-strain[7] associated with positioning of three α-picoline molecules around Ni(II) ion, which is already ligated with $TMPC^{2-}$ may be accounted for the failure to form Ni(TMPC).3α-pico.

†Electronic and IR spectral data in cm^{-1} throughout the paper.

The diffuse reflectance spectra of the complexes are characterised by two main bands in the regions 10,000-11,000 and 16,000-17,000 which may be assigned to the $^3A_{2g} \rightarrow {}^3T_{2g}(F)$ (ν_1) and $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (ν_2) transitions respectively in an idealised O_h symmetry. The relevant ligand field parameters, calculated through known relationships[8], namely Dq (980-1120 cm^{-1}), B(822-1113 cm^{-1}) and β (0.79-1.07), point to an average octahedral environment in the complexes[9]. The ν_2/ν_1 ratio of 1.6 gives additional support for the pseudo-octahedral nature of the species. In the present study, the transition $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (ν_3) expected for an octahedral Ni(II) complex could not be located (except in the case of α-picoline adduct where ν_3 is observed at 25,400); the position of ν_3 band, when computed[8], falls in the UV region (27,700—30,300) where it might be obscured by intense π-π^* transitions of the ligand or intense CT absorption; the origin of CT might be one from metal to ligand via the anti-bonding level of either the primary ligand (pyrazole derivative) or the secondary co-ligand (pyridine, bipyridyl etc.[10]).

The methanolic solutions of the pyridine and bipyridyl adduct show spectra indicating that there is no gross change in the stereochemistry of the complex species on dissolution as shown by the appearance of ν_1, ν_2 and ν_3 bands characteristics of pseudooctahedral Ni(II) species.

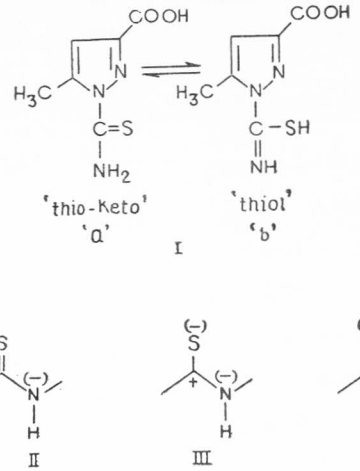
Ni(TMPC)NH₃.H₂O — The limited solubility and the subnormal magnetic moment (2.18 B.M.) of the ammonia adduct may result from the association between planar monomers in the solid state producing a quasi-octahedral coordination[11]. This is further substantiated by the reflectance spectrum which shows bands at 9,400 and 19,200 with a shoulder at 13,200 thereby indicating the co-existence of both paramagnetic octahedral and diamagnetic square-planar forms in the same compound in the solid state[12]. The solution spectrum of the compound in DMF (green solution) gives absorption bands at 10,050 (ν_1) 15,625 (ν_2) and 25,315(ν_3) typical of a pseudo-octahedral Ni(II), species; a stereochemical change of the complex is, therefore, proposed on dissolution in a donor solvent.

IR spectra — The characteristic band frequencies of the primary ligand ($TMPCH_2$) (with probable assignments[13-19]) together with the major changes in its metal complexes are as follows : The absence of any S-H band around 2600-2550 in the IR spectrum of the free ligand excludes the possibility of the existence of its thiol form (Ib) at least in the solid state.

The spectra of the metal complex are in general, complicated probably due to the presence of additional heterocyclic molecules as co-ligands. However, a careful scrutiny makes possible the following meaningful observations :

(i) The broad diffused bands at ~3400-3270 region, assignable to νNH + ν OH suggest extensive intra and/or intermolecular hydrogen bondings in the mixed complex species.

(ii) The newly developed bands around 2100 in all the metal complexes may be ascribed to



νC...N arising out of the participation of the thiocarbamyl residue in complex formation through the enolised thiol form of the ligand[18,19].

(iii) The $\nu_{as}COO^-$ of the free ligand at ~ 1725 has been found to shift towards lower frequency region, viz. around 1630 cm^{-1} in all the metal complexes indicating the participation of—COOH group of the primary ligand molecule in complex formation.

(iv) The role of the thiocarbamyl group (—NH-C = S) in complex formation is generally inferred from the consideration of the cannonical forms (II-IV).

The forms III and IV are more accessible due to higher polarisibility of the sulphur atom[20]. This indicates that the metal attachment through sulphur atom leads to a decrease in the thiocarbonyl stretching force and an increase of C-N frequency[21,22]. In the present case, IR bands around 1500 cm^{-1} in the metal complexes correspond to 1470 cm^{-1} band of the free ligand molecule which is assigned to ν_{as} N-C-N (B_1) of the thiosemicarbazide derivative[16]. The observed increase in frequency in the complexes may be due to the enhanced double bond character of C-N bond on complex formation through the thiol form[15,18,19]. In addition, the bands at 1430, 1310, 1120 and 895 which are attributed to rNH_2 or δNH_2 coupled with νC...S and/or νC...N suffer appreciable changes; the most notable change, however, occurs in the region 785 which is ascribed to νC...S of the ligand molecule. All these bands have either become weak and shifted towards lower frequeny side or have disappeared on complex formation; the observation indicates appreciable decrease in the bond order of C = S group on complexation to a metal through sulphur atom.

(v) The νN—N of the pyrazole ring system (coupled with δNH_2 appearing at 1015 ms and 980ms in the free ligand are found to shift towards higher frequency side (~ 1030) in the complexes suggesting the pyridine nitrogen atom of the pyrazole ring as a coordination site. X-ray crystallographic data on several pyrazole metal complexes[23-25] have also revealed this mode of bonding.

(vi) The characteristic vibrations of the secondary co-ligands, e.g. pyridine, methyl pyridines, bipyridyl and *o*-phenanthroline, have also been recognised[26,27] showing their presence in the respective adducts. A medium strong band at 990 and a strong band at 480 indicate the coordinated nature of the ammonia molecule[28] in $Ni(TMPC)NH_3.H_2O$. The broad nature of the band at ~3400 as well as the appearance of a strong band at ~850 do suggest the presence of coordinated water molecule[29] in $Co(TMPC)2H_2O$, whereas in all other mixed species the lattice water molecules are only present as has been substantiated by thermal data also.

It is conceivable, therefore, that the primary ligand molecule undergoes thione-thiol tautomerism in aqueous alcoholic solution and the thiol form (Ib) takes part in complexation through replacement of carboxylic and thiol hydrogens by metal ions resulting in the formation of M-O, M-N, (ring) and M-S bondings. A tacit support for such proposition is brought out more clearly from the far IR studies (recorded upto 200 cm^{-1}) on $Co(TMPC).2H_2O$ and $Ni(TMPC)NH_3.H_2O$ (species containing no additional N-heterocycle as co-ligand). The newly developed bands around 420 [435 (vs)/390 (w) for $Co(TMPC).2H_2O$ and 420 (s)/400 (ms) for Ni (TMPC) $NH_3.H_2O$], 350 [345(s) for Co (TMPC).$2H_2O$ and 355 (ms) for Ni(TMPC) $NH_3.H_2O$] and 270 [265 (w) for Co(TMPC).$2H_2O$ and 275 (ms) for $Ni(TMPC)NH_3.H_2O$] can be tentatively assigned to νM-O (ref. 30), νM—S-(ref. 31) and νM-N (pyrazole ring)[32] respectively.

TGA studies — The thermogravimetric analyses of some of the representative compounds reveal that the hydrated complexes suffer an initial loss of water molecules on heating around $110 \pm 5°C$ and the anhydrous species, undergo continuous mass loss giving no thermally stable intermediate. Finally the respective metal oxides are obtained around 350°C. Based on thermal stability of the complexes as manifested by the average decomposition temperature (220°C) as well as the percentage of mass loss before the onset of rapid decomposition, the following order can be worked out :

Co(II) complexes : bipy > γ-pico > H_2O ⩾ α-pico > py

Ni(II) complexes : β-pico > α-pico ⩾ NH_3 > py

The order cannot be correlated with the basicity of the coligands and may be ascribed to the steric interactions between the primary ligand molecule and the approaching secondary coligands.

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