# Cobalt(II), Nickel(II) & Copper(II) Complexes with Neutral & Deprotonated 5(3)-Methylpyrazole-3(5)-thiocarboxamide

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Cobalt(II), nickel(II) and copper(II) complexes of 5(3)-methylpyrazole-3(5)-thiocarboxamide (MPTAH) and its deprotonated anion (MPTA) have been synthesised and characterised in the solid state. Magnetic and electronic spectral data indicate that $M(MPTAH)_3X_2.nH_2O$ [X = Cl/Br/ClO$_4$/BF$_4$/$\frac{1}{2}$SO$_4$; M = Co/Ni; n = 0, 2], $Cu(MPTAH)_2X_2.nH_2O$ [X = Cl/NO$_3$/$\frac{1}{2}$SO$_4$/ClO$_4$; n = 0, 2] and $M(MPTA)_2.2H_2O$ [M = Co/Cu] are octahedral whereas $Ni(MPTA)_2.2H_2O$ is square-planar. The anions mostly retain their ionic character in case of the tris-species; some of them are coordinated in the bis-copper(II) complexes as inferred from IR data. The pyrazolyl ring nitrogen and the sulphur atom of the thioamide group appear to be the bonding sites in the complex species. The neutral bidentate (N-S) and monoprotic bidentate (N-S) function is envisaged in the complexes with the neutral and deprotonated ligand respectively.

In recent years, a substantial amount of work[1] has been done on the coordination chemistry of ligands having NS donor sites. The fungicidal and bactericidal action of thiopicolinamide[2] and the fact that such activities are often related to the chelation phenomenon have prompted us to synthesise and to investigate the coordination properties of the title ligand (I) as a part of our comprehensive programme[3] on the investigation of metal complexes of pyrazole-derived ligands.



Thio-keto                        Thiol

(I)
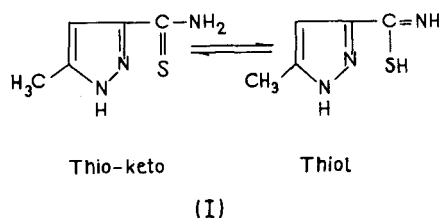
The ligand, 5(3)-methylpyrazole-3(5)-thiocarboxamide, was synthesised for the first time by the reaction of 5(3)-methylpyrazole-3(5)-carboxamide with phosphorous pentasulphide following the method adopted by Kornfield[4] for the preparation of N,N-diethyl thionicotinamide. The product was recrystallised from ethanol; m.p. 175°C [Found : C, 42.12; H, 4.62; N, 29.51; S, 22.01. Reqd. for $C_5H_7N_3S$: C, 42.55; H, 4.96; N, 29.78; S, 22.69%].

## Preparation of complexes

(A) Tris-complexes, $M(MPTAH)_3X_2.nH_2O$ [M = Co/Ni; X = Cl, Br, ClO$_4$, $\frac{1}{2}$SO$_4$, BF$_4$; n = 0,2 ]

An ethanolic solution ( ~ 30 ml) of $MX_2.nH_2O$ (0.01 mol) (in the case of metal sulphate water was used as the solvent) was added to a solution of the ligand (0.03 mol) in the same solvent ( ~ 25 ml). The resulting solution (pH ~ 4) was concentrated by heating on a water-bath and cooled to room temperature (25°C), when coloured microcrystalline compounds separated out (addition of cold ether was necessary for rapid crystallisation in some cases). The compound, in each case, was filtered off, washed with cold ether and dried over calcium chloride.

(B) Bis-complexes, $Cu(MPTAH)_2X_2.nH_2O$ [X = Cl, NO$_3$, $\frac{1}{2}$SO$_4$, ClO$_4$; n = 0,2 ]

An ethanolic solution ( ~ 25 ml) of $CuX_2.nH_2O$ (0.01 mol) (water was used as the solvent in case of $CuSO_4.5H_2O$) was added to a solution of the ligand (0.02 mol) in the same solvent. The resulting solution (pH ~ 4) was concentrated by heating on a water-bath and cooled to room temperature when a coloured microcrystalline compound separated out. It was collected and dried as before.

(C) Bis-complexes of the deprotonated ligand, $M(MPTA)_2.2H_2O$ [M = Co$^{II}$, Ni$^{II}$, Cu$^{II}$]

Alcoholic solutions ( ~ 25 ml) of the hydrated metal(II) chlorides (0.01 mol) and the ligand (0.02 mol, 25 ml) were mixed. On raising the pH of the solution to ~ 8 by the dropwise addition of 2N KOH, the desired compounds separated out, which were digested for some time by heating on a water-bath and then cooled to room temperature. The compounds were collected and dried as before.

Carbon, hydrogen and nitrogen were determined microanalytically. Cobalt content was estimated gravimetrically as anhydrous cobalt(II) sulphate except in the case of the perchlorate complex where the cobalt was estimated as cobalt(II)mercurithiocyanate. Nickel was estimated as nickel dimethylglyoximate and copper iodometrically. Sulphur was estimated as barium sulphate in the usual manner. The molar conductances, magnetic susceptibilities, electronic and IR spectra of the complexes were recorded as described earlier[5].

The analytical data, colour, effective magnetic moments and molar conductance values are given in Table 1. The complexes $M(MPTAH)_3X_2.nH_2O$ and $Cu(MPTAH)_2X_2.nH_2O$ are highly soluble in water,

Table 1—Physical Properties and Analytical Data of the Complexes

| Compound | Colour | Found (calc.), % | | | | $\Lambda_M$(ohm$^{-1}$ cm$^2$mol$^{-1}$) | $\mu_{eff.}$(B.M.) |
| | | Metal | N | S | Anion | | |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Co(MPTAH)$_3$Cl$_2$ | Reddish brown | 10.4 (10.6) | 22.6 (22.7) | 17.0 (17.3) | 12.5 (12.8) | 162.0 | 4.72 |
| Co(MPTAH)$_3$(ClO$_4$)$_2$ | Reddish brown | 8.4 (8.6) | 18.4 (18.5) | 13.6 (14.0) | 10.1 (10.4)* | 225.1 | 4.56 |
| Co(MPTAH)$_3$SO$_4$2H$_2$O | Reddish brown | 9.5 (9.6) | 20.3 (20.5) | 15.2 (15.6) | — | 63.7 | 5.01 |
| Co(MPTA)$_2$.2H$_2$O | Blackish brown | 15.6 (15.7) | 22.3 (22.4) | 16.7 (17.0) | — | 21.3*** | 4.68 |
| Ni(MPTAH)$_3$Cl$_2$ | Yellowish green | 10.4 (10.5) | 22.6 (22.8) | 16.9 (17.3) | 12.5 (12.8) | 224.2 | 2.98 |
| Ni(MPTAH)$_3$Br$_2$ | Yellowish green | 8.6 (8.7) | 19.2 (19.0) | 14.1 (14.5) | 23.9 (24.2) | 149.0 | 3.01 |
| Ni(MPTAH)$_3$(ClO$_4$)$_2$ | Greenish yellow | 8.4 (8.5) | 18.4 (18.5) | 13.8 (14.1) | 10.2 (10.4)* | 203.8 | 3.20 |
| Ni(MPTAH)$_3$(BF$_4$)$_2$ | Yellowish green | 8.7 (8.5) | 19.1 (19.2) | 14.2 (14.6) | — | 169.5 | 3.12 |
| Ni(MPTAH)$_3$SO$_4$ | Dirty green | 9.8 (10.0) | 22.0 (21.8) | 16.3 (16.6) | — | 24.6 | 2.95 |
| Ni(MPTA)$_2$.2H$_2$O | Yellow | 15.4 (15.5) | 22.2 (22.4) | 16.8 (17.1) | — | 15.2*** | Diamagnetic |
| Cu(MPTAH)$_2$Cl$_2$ | Light green | 15.1 (15.2) | 19.9 (20.1) | 15.0 (15.3) | 16.8 (17.0) | 179.0 | 1.86 |
| Cu(MPTAH)$_2$(NO$_3$)$_2$2H$_2$O | Green | 12.4 (12.6) | 22.0 (22.1)** | 12.3 (12.6) | — | 126.0 | 1.79 |
| Cu(MPTAH)$_2$SO$_4$.2H$_2$O | Green | 13.0 (13.2) | 17.4 (17.5) | 19.5 (20.1)† | — | 76.0 | 2.00 |
| Cu(MPTAH)$_2$(ClO$_4$)$_2$2H$_2$O | Deep green | 10.8 (10.9) | 14.5 (14.4) | 10.8 (11.0) | 12.0 (12.2)* | 183.0 | 1.90 |
| Cu(MPTA)$_2$.2H$_2$O | Grey | 16.5 (16.7) | 22.0 (22.1) | 16.7 (16.8) | — | 19.0*** | 1.77 |

*Percentage of chlorine; †Including sulphur present in sulphate; **Including nitrogen present in nitrate; ***Conductance in DMF

alcohol and all other common organic solvents. But the complexes M(MPTA)$_2$2H$_2$O containing the deprotonated ligand are practically insoluble in water, and ethanol but are soluble in donor solvents like DMF, DMSO, etc.

Molar conductances of $10^{-3}M$ methanol solutions of the presumably ionic species lie within the range 149-224 ohm$^{-1}$cm$^2$mol$^{-1}$ indicating their 1:2 electrolytic behaviour[6]. The lower conductance values in the case of sulphate complexes can be explained in terms of the partial release of the SO$_4^{2-}$ ions. The conductance values of M(MPTA)$_2$.2H$_2$O are in the range 15-24 ohm$^{-1}$cm$^2$mol$^{-1}$ in DMF, which indicate that they are practically non-electrolytes in this solvent.

The room temperature magnetic moment values of the present tris- and bis-cobalt(II) complexes fall in the range 4.65-5.01 B.M. (Table 1). The values, in most cases, are in good agreement with those (4.8-5.2 B.M.) observed for most of the high-spin octahedral cobalt(II) complexes[7]. A lower value, in some cases, may be indicative[8] of a spin-state equilibrium between $^4T_{1g}$ and $^2E_g$ states suggesting that the overall ligand field in the complex species is close to the cross-over region of $3d^7$ cobalt(II) ion[9].

The diffuse reflectance spectra of cobalt(II) complexes exhibit characteristic absorptions for the following transitions $^4T_{1g}(F) \rightarrow {}^4T_{2g}$ [$v_1$; 8800-9800 cm$^{-1}$] and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ [$v_3$; 18,500-18,800 cm$^{-1}$] suggesting an octahedral geometry for the complexes[10]. The ligand field parameters (calculated through the known relationships[11]), viz. $Dq$ (994-1055 cm$^{-1}$), $B$ (676-724 cm$^{-1}$) and $\beta$ (0.70-0.74) provide additional support for an overall pseudo-octahedral geometry for these complexes. No remarkable change is noted when the electronic spectra are recorded in

methanol solution. The solution spectra of the complexes are characterised by one principal band in the region 18,500-19,200 cm$^{-1}$, which can be recognised as the transition in $O_h$ symmetry. Somewhat higher values of the molar extinction coefficient ($\varepsilon = 50$-60) for the spectral bands of these complexes might be ascribed to a distortion from a regular octahedral structure[10].

The room temperature magnetic moment values of the nickel(II) complexes Ni(MPTAH)$_3$X$_2$ lie between 2.95 and 3.20 B.M.; the values are in good agreement with those reported for six-coordinate spin-free nickel(II) complexes[12]. The diffuse reflectance spectra of the tris-complexes display three bands at $\sim 10,200$, $\sim 17,200$ and $\sim 24,800$ cm$^{-1}$ which are due to the transitions $^3A_{2g} \rightarrow {}^3T_{2g}$ ($v_1$); $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ ($v_2$) and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ ($v_3$) respectively in an idealised $O_h$ symmetry[13]. The ligand field parameter $Dq$ (taken directly from $v_1$ transition) falls in the range 1020-1040 cm$^{-1}$ and $v_2/v_1$ lies between 1.68 and 1.71; these values are in fine agreement with a pseudo-octahedral nickel(II)[14]. The electronic spectral data of the tris-complexes in methanol are characterised by three transitions $v_1$ (10,200-10,900 cm$^{-1}$), $v_2$(17,200-19,600 cm$^{-1}$) and $v_3$(24,400-25,000 cm$^{-1}$) in an idealised $O_h$ symmetry. The molar extinction values of $v_1$ and $v_2$ (20-40) give an additional support to the octahedral geometry. But high extinction value (285-450) of the $v_3$ band may be due to the mixing of this band with charge transfer band originating probably from LMCT; this type of higher extinction value is also common in S-bonded Ni(II) complexes[15].

The yellow bis-complex of nickel(II), Ni(MPTA)$_2$.2H$_2$O, is diamagnetic; a square-planar geometry is, therefore, suggested for the complex. This suggestion is substantiated by the diffuse reflectance spectrum of the complex which shows distinct bands at 11,100; 19,200 and 23,800 cm$^{-1}$ which may be assigned to $v_1$, $v_2$ and $v_3$ transitions respectively in a square-planar $d^8$ environment[11]. The red solution obtained on dissolution of the complex in DMF does not show any significant change in its spectrum. It is conceivable, therefore, that the square-planar configuration is also retained in a donor solvent like DMF.

The room temperature magnetic moment values of Cu(MPTAH)$_2$X$_2$.nH$_2$O lie in the range 1.77-2.00 B.M. indicating that the copper(II) ion in these complexes is in a non-degenerate ground state[7]. The diffuse reflectance spectra of these complexes are characterised by a broad band in the region 13,500-14,300 cm$^{-1}$ in $O_h$ symmetry[11]. The $Dq$ values (670-720 cm$^{-1}$) are in good agreement with an octahedral structure. The electronic spectra of Cu(MPTAH)$_2$X$_2$.nH$_2$O in methanol and Cu(MPTA)$_2$.2H$_2$O in DMF are characterised by a main band around 13,500-14,900 cm$^{-1}$ which indicates that there is no appreciable change in the stereochemistry of the complexes on dissolution in a solvent. The high extinction coefficient values ($\varepsilon \approx$ 150) for the band are also expected for a ligand containing N-S donor system. The band that appears near 24,000 cm$^{-1}$ in case of Cu(MPTA)$_2$Cl$_2$ might be of charge-transfer type.

The IR spectrum of the ligand in KBr exhibits a broad band around 3340-3020 cm$^{-1}$ which is due to NH stretching vibration of the pyrazole ring and that of thioamide component mixed up together; a band at 1680-1640 cm$^{-1}$ is due to $\delta$ NH$_2$ coupled with the stretching vibration. An IR band at 1570 cm$^{-1}$ may be assigned to $v$ C = N of pyrazole ring. The strong band appearing at 1490 cm$^{-1}$ is the thioamide II band (due to coupling of N-H bending and C-N stetching modes), whereas the band at 1420 cm$^{-1}$ results from the coupling of $v$C = N and $\delta$NH. However, the band at 1290 cm$^{-1}$ is thioamide I band (due to symmetric $v$C = S vibration) and that at 830 cm$^{-1}$ is asymmetric $v$C = S stretching vibration[16,17]. The absence of any S-H band around 2600-2550 cm$^{-1}$ in the IR spectrum of the free ligand indicates that the ligand is present in thione form in the solid state[18].

The free ligand band at 1570 cm$^{-1}$ (due to $v$C = N of the pyrazole ring) is shifted to a higher wave number ($\Delta v = 10$-15 cm$^{-1}$) in the complexes suggesting that the tertiary (ring) nitrogen atom of the pyrazole moiety is a bonding site. In the tris-complexes of nickel(II) and cobalt(II), M(MPTAH)$_3$X$_2$.nH$_2$O, and the bis-complexes of copper(II), Cu(MPTAH)$_2$X$_2$.nH$_2$O, the $v$NH mode and the thioamide II band shift to higher frequency regions. This indicates that the thio-amide nitrogen does not take part in coordination. The positive indication of the coordination through sulphur comes mainly from the change in $v$C = S vibration. In the spectra of the complexes, the symmetric $v$C = S band i.e., the thioamide I band in the free ligand ($\sim 1290$ cm$^{-1}$) as well as $v$C = S asymmetric vibration ($\sim 830$ cm$^{-1}$) experienced negative shift [$\Delta v = 15$-50 cm$^{-1}$ and $\Delta v = 5$-20 cm$^{-1}$ respectively]. These data positively indicate the formation of the metal-sulphur bond on complexation[16]. The negative shift of thioamide I band and the positive shift of the thioamide II band might be reconciled in terms of a decrease in the bond order of >C = S and an increase in the bond order of C-N, respectively, both being due to coordination to a metal ion through sulphur. In complex species of the deprotonated ligand [M(MPTA)$_2$.2H$_2$O], the ligand behaves as a monoprotic bidentate one in its 'thiol' form. New bands which are absent in the far IR spectrum of the free ligand appear in the metal complexes at 350 and

$265$ cm$^{-1}$ which have been assigned to $\nu$M-S (ref. 19) and $\nu$M-N modes (ref. 20) respectively.

The diagnostic IR bands of the polyatomic anions indicate that the perchlorate group remains ionic in the tris-complexes [IR bands at 1150-1060 cm$^{-1}$ ($\nu_3$) and $620$ cm$^{-1}$ ($\nu_4$) are assigned to ionic perchlorate in $T_d$ symmetry[21]] while in the bis-Cu(II) species, Cu(MPTAH)$_2$(ClO$_4$)$_2$.2H$_2$O, it behaves as a monodentate ligand (i.e. bands at 1145, 1120, 1085 cm$^{-1}$ being attributed to the split components of $\nu$(Cl-O) in $C_{3v}$ symmetry[22]). This observation seems contradictory to its high molar conductance value, but it can be reconciled in terms of extensive solvolysis of the species in methanol. The nitrate in Cu(MPTAH)$_2$(NO$_3$)$_2$.2H$_2$O shows distinct bands at 1325, 1050 (split components of $\nu_3$ vibration) and 825 cm$^{-1}$ ($\nu_2$) suggesting monodentate nitrate in $C_{2v}$ symmetry[23]; this observation can also be explained as in the case of perchlorate. The appearance of a strong band around 1150-1050 cm$^{-1}$ in both bis- and tris-complexes ($\nu_3$) indicates an ionic sulphate in $T_d$ symmetry[24]. The ionic nature of the BF$_4$ group is ascertained by the appearance of a strong but very broad band in the region 1105-1035 cm$^{-1}$ ($\nu_3$ mode of BF$_4^-$ in $T_d$ symmetry[25]).

It appears, therefore, that the ligand 5(3)-methylpyrazole-3(5)-thiocarboxamide exhibits a neutral bidentate (NS) function in the tris-complexes M(MPTAH)$_3$X$_2$.nH$_2$O and bis-species, Cu(MPTAH)$_2$X$_2$.nH$_2$O while at higher $p$H ($\sim$8), the ligand shows a monoprotic bidentate NS character forming complexes of the type M(MPTA)$_2$.2H$_2$O.

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