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Synthesis & Characterization of Nickel(II) Complexes with Thiophene-2-Carboxyaldehyde Thiosemicarbazone

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Nickel(II) complexes of thiophene-2-carboxyaldehyde thiosemicarbazone (TATS-H) of general formulae $\text{Ni}(\text{TATS-H})_2\text{X}_2$, $\text{Ni}(\text{TATS-H})\text{X}_2$, $\text{Ni}(\text{TATS-H})\text{X}$ and $\text{Ni}(\text{TATS})_2$, where $\text{X} = \text{NO}_3^-$, Cl^- , Br^- , I^- , SCN^- , SO_4^{2-} and CH_3COO^- , have been prepared and characterised. Except $\text{Ni}(\text{ligand})_2$ (SCN)₂ and $\text{Ni}(\text{ligand})$ (SCN)₂, which show magnetic moments of 2.27 and 1.79 B. M., respectively, all the complexes are diamagnetic and thus square-planar. In pyridine solution they show magnetic moments in the range 2.92-3.47 B. M., apparently due to coordination of pyridine in axial positions.

PREPARATION and characterisation of transition metal complexes of thiosemicarbazones have received considerable attention recently. In this note we report the preparation and characterization of nickel(II) complexes of thiophene-2-carboxyaldehyde thiosemicarbazone (TATS-H). Complexes of the type $\text{Ni}(\text{TATS-H})_2\text{X}_2$, $\text{Ni}(\text{TATS-H})\text{X}_2$, $\text{Ni}(\text{TATS})\text{X}$ and $\text{Ni}(\text{TATS})_2$ [where $\text{X} = \text{NO}_3^-$, Cl^- , Br^- , I^- , SCN^- , $\frac{1}{2}\text{SO}_4^{2-}$ and CH_3COO^- , and TATS-H acts as a neutral bidentate ligand in its keto form] have been isolated and characterised. The deprotonated form of TATS-H, which arises through enolization in slightly alkaline solution, forms complexes of the type $\text{Ni}(\text{TATS})\text{X}$ and $\text{Ni}(\text{TATS})_2$. Spectral and magnetic measurements indicate that all the complexes are four-coordinated and of low-spin type having square-planar geometries.

Preparation of thiophene-2-carboxyaldehyde thiosemicarbazone (TATS-H) — Thiosemicarbazide (0.1 mol) was dissolved in 30 ml distilled water and 2 ml glacial acetic acid, and warmed on a steam-bath till a clear solution was obtained. Then, a hot solution of thiophene-2-carboxyaldehyde (0.1 mol) in 25 ml of absolute ethanol was added to it. The reaction mixture was refluxed on a steam bath for 30 min and cooled. The product was filtered off by suction and purified by recrystallisation from 1:1 ethanol, yield 65%. [Found : C, 38.93; H, 3.80; N, 22.65; S, 34.64. Calc. : C, 38.89; H, 3.81; N, 22.68; S, 34.62%].

Preparation of the chelates : (i) $\text{Ni}(\text{TATS-H})_2\text{X}_2$ ($\text{X} = \text{NO}_3^-$, Cl^- , Br^- , I^- , SCN^- , $\frac{1}{2}\text{SO}_4^{2-}$ and CH_3COO^-) — To a hot solution of the ligand (0.02 mol) in ethanol (50 ml) was added a hot clear solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.01 mol) in ethanol (20 ml) and the reaction mixture was refluxed for 20 min. $\text{Ni}(\text{TATS-H})_2\text{Cl}_2$, which separated on cooling, was filtered off and recrystallized from ethanol. The $\text{Ni}(\text{TATS-H})_2(\text{NO}_3)_2$ chelate was similarly prepared starting with $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The corresponding bromo, iodo and thiocyanato chelates were prepared meta-thetically from the reaction of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.01 mol) in ethanol (20 ml) with TATS-H (0.02 mol) in ethanol (20 ml) in the presence of NH_4Br , NH_4I or NH_4SCN (0.025 mol). $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ were taken in water instead of ethanol to prepare the $\text{Ni}(\text{TATS-H})_2\text{SO}_4$ and $\text{Ni}(\text{TATS-H})_2(\text{CH}_3\text{COO})_2$ chelates respectively.

(ii) $\text{Ni}(\text{TATS-H})\text{X}_2$ ($\text{X} = \text{NO}_3^-$, Cl^- , Br^- , I^- , SCN^- , $\frac{1}{2}\text{SO}_4^{2-}$ and CH_3COO^-) — A hot solution of (TATS-H) (0.01 mol) in ethanol (30 ml) was added to a hot clear solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.015 mol) in ethanol (20 ml) and the reaction mixture was refluxed on a water-bath for 20 min. $\text{Ni}(\text{TATS-H})\text{Cl}_2$, which separated on cooling, was filtered and recrystallized from ethanol. The $\text{Ni}(\text{TATS-H})(\text{NO}_3)_2$ chelates were prepared similarly using $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The corresponding bromo, iodo and thiocyanato chelates were prepared by adding a solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.01 mol) in ethanol (20 ml) to a solution of ammonium bromide, iodide or thiocyanate (0.025 mol) in ethanol (10 ml), boiling the reaction mixture for 10 min on a water-bath, concentrating it by evaporation, then cooling it in an ice-bath and finally filtering off the precipitated ammonium nitrate. To the hot clear filtrate, a solution of TATS-H (0.01 mol) in ethanol (20 ml) was added and the reaction mixture was refluxed for 30 min. On cooling, the complex separated out, which was filtered and recrystallized from ethanol. The sulphate and acetate complexes were prepared by taking the metal ion solution in water.

(iii) $\text{Ni}(\text{TATS})\text{X}$ ($\text{X} = \text{NO}_3^-$, Cl^- , Br^- and I^-) — A hot solution of TATS-H (0.01 mol) in ethanol (30 ml) was added to a hot clear solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.015 mol) in ethanol (20 ml) in presence of one equivalent of NaOH and the reaction was refluxed for 20 min on a water-bath. $\text{Ni}(\text{TATS})\text{Cl}$, which separated on cooling, was filtered and recrystallized

from ethanol. The Ni(TATS)NO_3 chelate was prepared similarly using $\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The corresponding bromo, iodo and thiocyanato chelates were prepared metathetically in presence of one equivalent of NaOH.

(iv) Ni(TATS)_2 — A hot solution of TATS-H (0.02 mol) in ethanol (50 ml) was added to a hot solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.01 mol) in ethanol (20 ml) in the presence of two equivalents (excess) NaOH and the contents were refluxed on a water-bath for 20 min. On cooling the contents, a dark-green compound separated out. It was filtered and recrystallized from ethanol.

The room temperature magnetic susceptibility measurements were carried out on a Gouy balance using $\text{Hg[Co(NCS)}_4]$ as the calibrant. Diamagnetic corrections were applied using Pascal's constants. Solution spectra were recorded in methanol on a Beckman DU spectrophotometer using 1 cm quartz cells. Infrared spectra were recorded on a Perkin-Elmer 621 spectrophotometer in KBr. All the nickel analyses were carried out using an atomic

absorption instrument. Molecular conductances were measured on a Leeds and Northrup Electrolytic Conductivity Bridge at 35°C using 0.001 M solutions in methanol.

By varying the conditions of isolation, four different types of metal complexes, $\text{Ni(ligand-H)}_2\text{X}_2$, Ni(ligand-H)X_2 , Ni(ligand)X and Ni(ligand)_2 have been synthesized (Table 1).

$\text{Ni(TATS-H)}_2\text{X}_2$ and Ni(TATS-H)X_2 — In absolute ethanol, reaction of TATS-H with Ni(II) gives $\text{Ni(TATS-H)}_2\text{X}_2$ when excess of ligand is used (i. e. L : M is 2 : 1), and Ni(TATS-H)X_2 is formed when excess of metal salt is used (i.e., L:M is 2:3). All the complexes are diamagnetic except $\text{Ni(TATS-H)}_2(\text{SCN})_2$ and Ni(TATS-H)(SCN)_2 which have the magnetic moment values of 2.27 and 1.79 B. M. respectively. These magnetic moments may be due to the formation of octahedral complexes like $\text{Ni(TATS-H)}_2(\text{SCN})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Ni(TATS-H)(SCN)}_2 \cdot 2\text{H}_2\text{O}$. The reason for low magnetic moment values as compared to those expected for octahedral complexes is uncertain although the measurements were

TABLE 1 — ELEMENTAL ANALYSES, ELECTRONIC CONDUCTIVITY AND MAGNETIC MOMENTS OF NICKEL(II) CHELATES

| Complex/Colour | Found (Calc), % | | | | | ΔM (ohm^{-1} mol^{-1} cm^{-2})* | μ_{eff} at 298°K in pyridine solution |
|---|------------------|------------------|----------------|------------------|------------------|---|---|
| | Metal | C | H | N | S | | |
| $\text{Ni(TATS-H)}_2(\text{NO}_3)_2$ (Green) | 10.57 (10.82) | 26.10 (26.14) | 2.17 (2.19) | 20.38 (20.33) | 23.24 (23.27) | 110.85 | 3.14 |
| $\text{Ni(TATS-H)}_2\text{Cl}_2$ (Green) | 11.82 (11.79) | 28.80 (28.93) | 2.39 (2.43) | 16.93 (16.87) | 25.91 (25.75) | 97.54 | 3.23 |
| $\text{Ni(TATS-H)}_2\text{Br}_2$ (Pale-green) | 10.03 (10.00) | 24.53 (24.55) | 2.10 (2.06) | 14.35 (14.32) | 21.88 (21.85) | 79.51 | 3.43 |
| $\text{Ni(TATS-H)}_2\text{I}_2$ (Pale-green) | 8.51 (8.62) | 21.11 (21.16) | 1.79 (1.78) | 12.36 (12.34) | 18.85 (18.83) | 99.94 | 3.21 |
| $\text{Ni(TATS-H)}_2(\text{SCN})_2 \cdot 2\text{H}_2\text{O}$ (Greenish-yellow) | 11.32 (11.50) | 32.91 (32.94) | 2.72 (2.73) | 21.85 (21.98) | 37.70 (37.75) | 119.08 | 3.09 |
| $\text{Ni(TATS-H)}_2\text{SO}_4$ (Green) | 11.40 (11.22) | 27.52 (27.54) | 2.34 (2.31) | 16.08 (16.05) | 30.61 (30.64) | 90.65 | 3.20 |
| $\text{Ni(TATS-H)}_2(\text{CH}_3\text{COO})_2$ (Light-green) | 10.71 (10.77) | 35.37 (35.24) | 3.31 (3.33) | 15.40 (15.41) | 23.55 (23.52) | 108.44 | 3.29 |
| $\text{Ni(TATS-H)(NO}_3)_2$ (Blackish-green) | 16.20 (16.00) | 19.67 (19.64) | 1.66 (1.65) | 19.10 (19.08) | 17.51 (17.48) | 2.17 | 3.02 |
| Ni(TATS-H)Cl_2 (Green) | 18.78 (18.20) | 22.98 (22.96) | 1.91 (1.93) | 13.42 (13.39) | 20.39 (20.43) | 10.61 | 3.41 |
| Ni(TATS-H)Br_2 (Brownish-green) | 14.65 (14.58) | 17.81 (17.89) | 1.52 (1.50) | 10.41 (10.43) | 15.96 (15.92) | 00.03 | 3.47 |
| Ni(TATS-H)I_2 (Pale-green) | 11.75 (11.82) | 14.49 (14.51) | 1.25 (1.22) | 8.48 (8.46) | 12.88 (12.91) | 15.35 | 3.46 |
| $\text{Ni(TATS-H)(SCN)}_2 \cdot 2\text{H}_2\text{O}$ (Greenish-yellow) | 17.90 (17.99) | 29.49 (29.42) | 2.58 (2.55) | 21.49 (21.45) | 39.38 (39.28) | 30.20 | 3.08 |
| Ni(TATS-H)SO_4 (Yellowish-green) | 17.39 (17.39) | 21.15 (21.25) | 1.83 (1.78) | 12.21 (12.39) | 28.15 (28.37) | 6.65 | 2.95 |
| $\text{Ni(TATS-H)(CH}_3\text{COO)}_2$ (Light-green) | 16.41 (16.26) | 33.12 (33.26) | 3.33 (3.35) | 11.85 (11.64) | 17.73 (17.76) | 19.71 | 3.18 |
| Ni(TATS)NO_3 (Green) | 19.50 (19.31) | 23.62 (23.71) | 1.69 (1.66) | 18.52 (18.43) | 21.12 (21.10) | 5.17 | 2.99 |
| Ni(TATS)Cl (Green) | 21.32 (21.16) | 25.92 (25.97) | 1.80 (1.82) | 15.25 (15.15) | 23.12 (23.12) | 11.89 | 3.10 |
| Ni(TATS)Br (Green) | 18.11 (18.24) | 22.43 (22.39) | 1.51 (1.57) | 13.12 (13.06) | 19.72 (19.92) | 8.86 | 2.92 |
| Ni(TATS)I (Brown) | 15.87 (15.92) | 19.41 (19.54) | 1.35 (1.37) | 11.28 (11.39) | 17.49 (17.39) | 8.03 | 3.33 |
| Ni(TATS)_2 (Dark-green) | 13.67 (13.81) | 16.87 (16.95) | 2.43 (2.37) | 19.70 (19.77) | | 14.32 | 3.29 |

* ΔM values were recorded for 10^{-3}M solutions in methanol.

repeated several times on specimens giving good analysis.

The magnetic moments of these nickel(II) complexes when taken in pyridine solution, have been found to be in the range 2.92-3.47 B. M. which clearly reflect the change of stereochemistry from planar to octahedral, most probably due to the axial coordination of two pyridine molecules to each complex molecule.

Electrical conductivity measurements in MeOH (Table 1) show that the complexes behave as 1:2 electrolytes⁸ and may exist predominantly as neutral Ni(TATS-H)₂X₂ molecules. The relatively high conductance values of the 1:2 complex solutions suggests the formation of Ni(TATS-H)₂²⁺ ion. The mono ligand chelates, Ni(TATS-H)X₂ are completely dissociated in methanol and their solutions behave as 1:2 electrolytes⁸.

Electronic spectra of the complexes in methanol solution are characteristic of square-planar nickel(II). Bands corresponding to *d-d* transitions, ¹A_{1g} → ¹B_{1g} and ¹A_{1g} → ¹E_g are observed at ~16000 and ~19000 cm⁻¹, respectively in all cases. In addition, there are some strong charge-transfer absorptions.

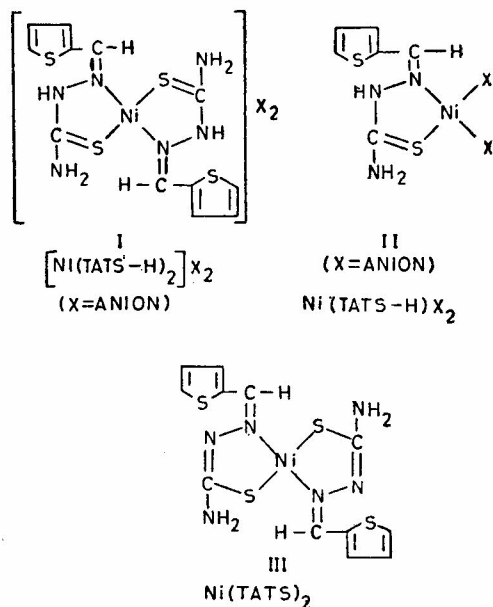
Ni(TATS)X and *Ni(TATS)₂* — The IR -spectra of these chelates are different from that of the neutral parent organic ligand. The Ni(II) chelates are diamagnetic which fact suggests square-planar structures for them. Their solution electronic spectra also confirm such an arrangement.

The neutral bis-ligand chelate, Ni(TATS)₂ was isolated from the reaction of TATS-H with nickel(II) acetate in methanol. Its IR spectrum is similar to the spectra of Ni(TATS)X chelates, showing that the thiosemicarbazone molecule acts as a uninegative bidentate ion. Both magnetic and spectral properties of this chelate favour a square-planar structure.

Metal complexes of thiosemicarbazone have been studied in good detail and it has been shown¹⁻³ that the νC=S mode has considerable contribution towards a band in the region 805-830 cm⁻¹, and it also contributes to a band at ~1100 cm⁻¹ where it is coupled with the N-C-N stretching⁴, or N-N stretching and N-C-N deformation vibrations⁵.

In TATS-H, νC=S occurs at 835 cm⁻¹ with a shoulder at 860 cm⁻¹. On complex formation this band is shifted to lower wave numbers by 50-90 cm⁻¹. The band is often split or has a pronounced shoulder in a manner similar to that already observed for the nickel(II) complexes of other thiosemicarbazones⁶. This splitting may be related to a small difference between the two Ni-S band lengths⁹.

Formation of a thiosemicarbazone not only leads to the disappearance of the band due to δNH₂ of the hydrazinic group of thiosemicarbazide but also causes the amide-II band at 1605 cm⁻¹ to shift to lower wave numbers. This kind of shift has been attributed to the presence of the electron withdrawing substituent on the hydrazinic nitrogen⁷. However, on complex formation the band shifts to higher wave numbers and often splits, such a shift to higher wave number is probably the result of the increase in the



multiplicity of the C-N bond resulting in a stronger N-H bond in the amide group. Thus, it seems that contrary to Wiles' assumption⁷, substitution on the hydrazinic nitrogen in thiosemicarbazide causes electron release which counteracts the effect of the electronegativity of sulphur and decreases the probability of multiplicity in the C-N bond of the amide group.

The thiocyanate group in Ni(TATS-H)(SCN)₂·2H₂O displays bands at 2060(s), 820(s) and 480(b) cm⁻¹ assignable to ν(C=N), ν(C-S) and σ(NCS) modes, respectively, of N-bonded thiocyanate¹⁰. The spectrum of Ni(TATS-H)₂(SCN)₂·2H₂O shows new bands at 2050(s), 750(m) and 470(b) cm⁻¹, corresponding to the presence of ionic thiocyanate. The spectrum of Ni(TATS-H)(NO₃)₂ exhibits νNO at 1425 (m) and 1300(m) cm⁻¹. These bands show that the nitrate group acts as a unidentate ligand. The spectrum of Ni(TATS-H)SO₄ shows four bands at 1160(m), 1095(m), 1040(m) and 970(m) cm⁻¹ which may be assigned to the sulphato group acting as a bridging bidentate ligand. The spectrum of Ni(TATS-H)₂SO₄ shows corresponding ionic sulphato group bands at 1145(b) and 965(vw)¹⁰.

It is difficult to assign the metal-ligand and metal-halide vibrations unambiguously, since many bands are present between 250 and 400 cm⁻¹ in the free ligand.

Structures I, II and III may be assigned to the complexes of the type Ni(TATS-H)₂X₂, Ni(TATS-H)X₂ and Ni(TATS)₂ respectively.

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Cobalt(II), Nickel(II), Copper(II), Zinc(II) & Cadmium(II) Complexes with Analgin

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and

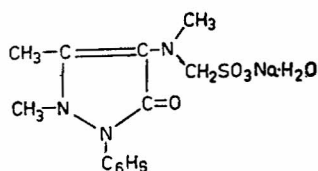
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Complexes of the types $M(AG)_2$ and $Cd(AGNa)_2$, where $M = Co(II), Ni(II), Cu(II)$ or $Zn(II)$; $X = Cl^-, Br^-$ or I^- ; and $AGNa =$ analgin, have been synthesised and characterised on the basis of elemental analyses, molar conductance, magnetic measurements, electronic, electron spin resonance and infrared spectral studies.

ANALGIN (1-phenyl-2,3-dimethyl-5-pyrazolone-4-methylaminomethane sulphonate sodium monohydrate), I, is a potent nonsalicylate analgesic, antipyretic, antiinflammatory and antirheumatic agent¹. Since the biological activity of drugs is reported^{2,3} to be considerably affected on coordination with metal ions, we have undertaken the preparation and characterisation of the complexes of $Co(II)$, $Ni(II)$, $Cu(II)$ and $Zn(II)$ with (I) and the results are reported in this note.



(I)

Metal(II) halides were AR grade (BDH) chemicals. Analgin (in fine powder form) was obtained as a gift sample from IDPL Hyderabad. These chemicals were used as such without further purification.

$Co(II)$, $Ni(II)$, $Cu(II)$, $Zn(II)$ and $Cd(II)$ complexes with analgin were prepared by refluxing ethanolic

solutions of metal(II) halides or metal(II) perchlorates and analgin for about 1/2 hr in 1 : 2 metal : ligand ratio. The complexes were recrystallised from ethanol and dried over fused calcium chloride. Complexes with $Hg(II)$ could not be studied due to their instability. The metal ions, halide ions and nitrogen were analysed by standard procedures⁴. Physico-chemical data were recorded using ECIL conductivity bridge, Cahn magnetic balance, Perkin Elmer ESR, IR 621 and Cary 14 spectrophotometers.

$Co(II)$, $Ni(II)$ and $Cu(II)$ complexes with analgin are coloured, soluble in water and methanol but insoluble in non-polar organic solvents. $Cd(II)$ complexes are soluble in dimethylformamide also. All the complexes melt between 240 and 270°C. The molar conductance data of the complexes in water show their electrolytic nature^{5,6}. Colour of the aqueous or ethanol solutions changes on keeping due to partial dissociation of the complexes in solution suggesting weak metal-ligand bonds. The molar conductance data of $Cd(II)$ complexes in dimethylformamide suggest their non-electrolytic nature (Table I).

The room temperature magnetic moments for $Co(II)$, $Ni(II)$ and $Cu(II)$ complexes (Table 1) are found to be in the range expected for the spin-free octahedral stereochemistry^{7,8}. The UV spectrum of analgin (recorded in nujol) shows bands at 44843, 41666, 37037 and 30487 cm^{-1} . In all the complexes, these intra-ligand bands show bathochromic shift. $Co(II)$ -analgin complex shows electronic spectral bands at 8333, 20000 and 22222 cm^{-1} which may be assigned to the transitions ${}^4T_{1g} \rightarrow {}^4T_{2g}(F)$, ${}^4A_{2g}(F)$ and ${}^4T_{1g}(P)$ respectively. The values of $10Dq$, Racah parameter (B), nephelauxetic parameter (β), ν_2/ν_1 and the ligand field stabilisation energy are 7114 cm^{-1} , 1148.2 cm^{-1} , 1.03, 2.40 and 16.26 kcal/mol respectively. These features are characteristic of $Co(II)$ in an octahedral field-. The complex, $Ni(AG)_2$, shows three electronic spectral bands at 9645, 15384 and 25000 cm^{-1} assigned to $3A_{2g}(F) \rightarrow 3T_{2g}(F)$, $3T_{1g}(F)$ and $3T_{1g}$ transitions respectively. These assignments are characteristic of octahedral (O_h)

TABLE 1 — ANALYTICAL DATA OF $Co(II)$, $Ni(II)$, $Zn(II)$ AND $Cd(II)$ COMPLEXES WITH ANALGIN

| Complexes | m.p./ dec.p. (°C) | Found (Calc), % | | | ΔM in water | μ_{eff} (B.M.) |
|----------------|-------------------------|------------------|------------------|------------------|---------------------------|-----------------------|
| | | Metal | Halide | N | | |
| $Co(AG)_2$ | 240 | 8.38 (8.69) | — | 12.40 (12.37) | 230 | 4.94 |
| $Ni(AG)_2$ | 252 | 8.42 (8.69) | — | 12.37 (12.37) | 244 | 3.12 |
| $Cu(AG)_2$ | 255 | 9.26 (9.22) | — | 12.42 (12.30) | 236 | 1.76 |
| $Zn(AG)_2$ | 240 | 9.56 (9.49) | — | 12.37 (12.26) | 260 | — |
| $Cd(AGNa)Cl_2$ | 245 | 21.75 (21.71) | 13.92 (13.76) | 8.18 (8.18) | 391 | — |
| $Cd(AGNa)Br_2$ | 243 | 18.64 (18.51) | 26.54 (26.45) | 6.72 (6.94) | 386 | — |
| $Cd(AGNa)I_2$ | 247 | 16.38 (16.02) | 35.48 (36.34) | 6.24 (6.01) | 397 | — |

*in DMF