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THE PREPARATION, PROPERTIES OF MAGNETICALLY-NORMAL AND HIGH-SPIN NITROGEN-DONOR COMPLEXES OF CHROMIUM(II).

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Abstract

Nitrogen-donor complexes [1] $[Cr(tpam)_2]Br_2.\ 5H_2O$, $[Cr(tpam)I_2].\ 7H_2O$ and $[CrCl_2(ddad)]$ where tpam = tri(2-pyridy)amine and ddad = 3,6-dimethyl-1,8-(3,5-dimethyl-I-Pyrazolyl)-3, 6- diazaoctane are magnetically-normal and high-spin and do not have polymeric bridged structures.

1. Introduction

Several complexes [I] of tri(2-pyridyl)amine with chlorides and bromides of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Pd(II), Rb(II),Ir(II) such as $[Mn(tpam)Cl_2]$, $[Co(tpam)_2X_2]$ and $[Cu(tpam)_2][CuX_4]$ X = Cl or Br were prepared by the addition of ligand to metal in 1:1 molar ratio and their structures were discussed. Terdentate tri(2-pyridyl)amine is recognised as a strong-field ligand (Δ = 12,820 cm^{-1} with respect to Ni(II)) thus indicating that strong conjugation between the aromatic centres in polypyridyl ligands is not a prerequisite for high ligand field strength.

Kulsaingam and Mc Whinnie [2] have prepared compounds of bivalent cobalt, nickel and copper nitrates and thiocyanates with tri(2-pyridl) amine and di(2-pyridyl)phenylamine. The compounds are $[M(tpam)_2(NO_3)_2]$ (M = Co or Cu), $[M(tpam)_2](NO_3)_2$,(M = Co or Ni), $[Co(tpam_2)][CoX_4]$, (X = NO_3 or NCS), $[Ni(tpan)(H_2O)_2NO_3]$, $[Cu(tpam)(NO_3)I]$, $[M(tpam)_2(NCS)_2]$, M = Co or Ni, $[Ni(tpam)\ (NCS)_2]$ and $[CuL(CNS)_2]$ (L = tpam or dppa). The spectra of the compounds are discussed in terms of their probable structures and in addition evidence is presented to show that three possible linkage isomers of $[CuL(SCN)_2]$ have been prepared. In addition, several complexes of tri(2-pyridyl)amine with iron(II) perchlorate, chloride and bromide were prepared and their spectra were extensively discussed[3].

Haanstra et al [4] have isolated several compounds of the ligands 3,6-dimethyl-1,8-(3, 5-dimethyl-I-pyrazoly)-3,6-diazaoctane (ddad) and 1. 4-bis(2-ethy1-3, 5-dimethyl-1-pyrazolyl))-piprazine (bedp): M = Cu, Ni, M (ddad) $(BF4)_2$, $Co(ddad)(H_2O)\ (BF_4)_2$, $(M_2(ddad)Cl_4$, M = Co, Ni, Cu, Zn, $Co_3(ddad)_2(NCS)_6$ and $Cu_2(ddad)(NCS)_3$. The coordination by the ligand is square planar, while $Ni(ddad)(NCS)_2$contains additional trans-coordination thiocyanate anions. The coordination of the copper atoms in both molecules is intermediate between

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tetrahedral and square planar. The chloride compounds are except for Ni(II), all dinuclear with MN_2Cl_2 chromophores. The nickle(II) compound contains square planar $(Ni(ddad)^{2+}$ cations and tetrahedral $NiCl_4^{2-}$ anions. The thiocyanate compound of Ni(II), which is isomorphous with the corresponding Zn(II) compound, has octahedral chromophores. The cobalt compound crstallizes as $[Co(ddad)(NCS)_2][Co(NCS)_4]$ with five-coordinate cobalt in the cation. With copper thiocyanate ddad forms the mixed-valence compound $Cu_2(ddad)(NCS)_3$, containing, $[Cu(ddad)]^{2+}$ and $[Cu(NCS)]_3^{2-}$ ions.

2. Experimental

2.1 Preparation of Tri(2-pyridyl) amine

A mixture of 2-aminopyridine (9.00 g, 0.09 mole), 2-bromopyridine (25 g, 0.15 mole), powdered potassium carbonate (20 g), copper bronze (0.5 g), a trace of potassium iodide and pure dry mesitylene (50 cm3) was boiled under reflux for 16 hours (oilbath at 150-160^{O}C)[5]. The contents of the flask were then distilled with steam to remove mesitylene and unchanged bromopyridine and aminopyridine. There remained in the distillation flask a brown liquid, which partly solidified to a brown amorphous solid on cooling. The contents were extracted with chloroform (50 cm^3) and the brown residue obtained after evaporation of the chloroform was recrystallised from a mixture of benzene and hexane, after treatment with decolourizing charcoal (Yield 30%). Anal. Found, C, 72.40; H, 4.75; N, 22.21; Calc. for, $C_{15}H_{12}N_4$, C, 72.55; H, 4.87; N, 22.58%

2.2 Dibromobis(tri(2-pyridyl)amine)chromium(II) pentahydrate

Chromium(II) bromide hexahydrate (0.64 g, 0.002 mole) was dissolved in absolute ethanol (50 cm^3). To this was added, tri(2pyridyl)amine (1.00 g, 0.004 mole) and the reaction mixture was heated until all the solid dissolved. The dark green solution was allowed to cool in a refrigerator, but no solid was obtained, therefore, the solvent was evaporated under vacuum. The greenish brown compound obtained was washed with diethylether and dried under vacuum for three hours. It turned green in a few minutes in air (Yield 75%). Anal Found, C, 45.56;H,4.97; N, 14.87%; Calc. for. $C_{30}H_{34}N_8O_5CrBr_2$, C, 45.12; H, 4.29; N,14.03%.

2.3 Diiodo(tri(2-pyridyl)amine)chromium(II) heptahydrate

Chromium(II) iodide hexahydrate (2.80 g, 0.006 mole) was dissolved in absolute ethanol (50 cm^3). To this was added tri(2-pyridyl)amine (0.70 g, 0.002 mole) which dissolved on heating. The dark green solution was allowed to cool and a very small amount of dark yellow solid appeared. The solution was then kept in a refrigerator, but no additional product appeared. Therefore, the solution was concentrated to dryness and the dark yellow compound scraped out in the nitrogen box. It turned green in a few minutes in air (Yield 80%). Anal. Found, C, 15.56; H, 3.89; N, 4.42; Cr, 9.25; Calc. for, $C_{15}H_{42}N_4O_{15}Cr_2I_4$; C,15.93; H, 3.70; N, 4.90; Cr, 9.20%

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2.4 Preparation of [$CrCl_2$(ddad)]

Anhydrous chromium(II) chloride (0.17g, 0.0057 mole) was suspended in acetonitrile (25 cm^3). To this was added a solution of a liganed 3,6-dimethyl-1,8-(3,5-dimethyl-I-pyrazolyl)-3,6-diazaoctane(ddad) (1.91g, 0.0057 mole) in acetonitrile (30 cm^3) and the solution was heated to reflux for two hours. After cooling, the reaction mixture was concentrated to half volume. A small amount of green product was filtered off, dried and discarded because it contained some white impurity.

The blue filtrate was concentrated to dryness under vacuum and the blue crystalline compound was scraped out in the nitrogen box. It turned dark green in a few minutes in air (Yield 68%). Anal. Found C, 47.72; H, 7.56; N, 18.09; Calc. for, $C_{18}H_{32}N_6CrCl_2$; C, 47.46, H, 7.08; N, 18.45%.

3. Results and Discussions

3.1 Magnetic Properties

The variation with temperature of the atomic susceptibility (χ_A) and effective magnetic moments (μ_{eff}) of the complexes over the range 90-293°K are shown in table 3.1. Typical examples are plotted in Figure 3.1.

The complexes [$Cr(tpam)_2$]Br_2. $5H_2O$ and [Cr(tpam)I_2]. $7H_2O$ have room temperature megnetic moments of 5.00 and 4.84 B.M. respectively, which are very close to the spin-only value and do not change very much on lowering the temperature. The magnetic behaviour suggests that both compounds are magnetically-normal and high-spin and do not have polymeric bridged structures. The magnetic moment of the compound [$CrCl_2$(ddad)] at room temperature is 4.34 B.M. and it does not vary significantly with temperature. It appears that the compound is magnetically-dilute octahedral mononuclear chromium(II) complex but the reason for the slightly low moment is not known.

3.2 Infrared and Far Infrared Spectra

Detailed spectra of tri(2-pyridyl)amine complexes in the region 4000-600 cm^{-1} have not been given because they just show bands due to the organic ligands. Far infared spectra of [Cr(tpam)]Br_2 $5H_2O$ which did not show ν(Cr-Br) band which shows that there is no coordination of bromide. However, the ν(Cr-I) stretching bands were not observed because they are out of the range of the spectrophotometer. Far infrared spectra of the [$CrCl_2$(ddad)] show band at 265 cm^{-1} which is assigned to ν(Cr-Cl) for the complex.

3.3 Diffuse Reflectance Spectra

The diffuse reflectance spectra of [Cr(tpam)I_2], $7H_2O$ recorded over the range 2000 to 350 nm. The position in cm^{-1} (nm) show very broad band near 12000 cm^{-1} i.e 11628(860)br.The position and bredth of the band suggest that the chromium(II) is mainly coordinated to nitrogen-donor in distorted environment and the band at 27027(370)m which may be due to enternal transitions.

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Table 3.1

Compound	T (K)	χ_A x10^6	$1/\chi_A$ x10^{-1}	μ_{eff} (B.M)
$[Cr(tpam)I_2]\ 7H_2O$	293	10012	9.98	4.84
	265	10820	9.24	4.78
	230	12620	7.92	4.81
	200	14494	6.90	4.81
	165	16983	5.88	4.73
	136	20584	4.85	4.73
$\theta = 8^0$	105	26052	3.83	4.67
Diamagnetic correction = -228 c.g.s units per mole				
$[Cr(tpam)_2[Br_2.\ 5H_2O$	293	10710	9.33	5.00
	265	12057	8.29	5.05
	230	13538	7.38	4.99
	200	15766	6.34	5.02
	165	18314	5.46	4.91
	136	22663	4,41	4,96
	105	29213	3.42	4.95
$\theta = 4^0$	90	33148	3.01	4.88
Diamagnetic correction = --292 c.g.s units per mole				
$[CrCl_2(ddad)]$	293	8075	12.38	4.34
	265	8864	11.28	4.33
	230	10080	9.92	4.30
	200	11640	8.59	4.31
	165	13835	7.22	4.27
	136	16882	5.92	4.28
	105	21825	4.58	4.28
$\theta = 4^o$	90	24982	4.00	4.24
Diamagnetic correction = - 348 c.g.s. units per mole				

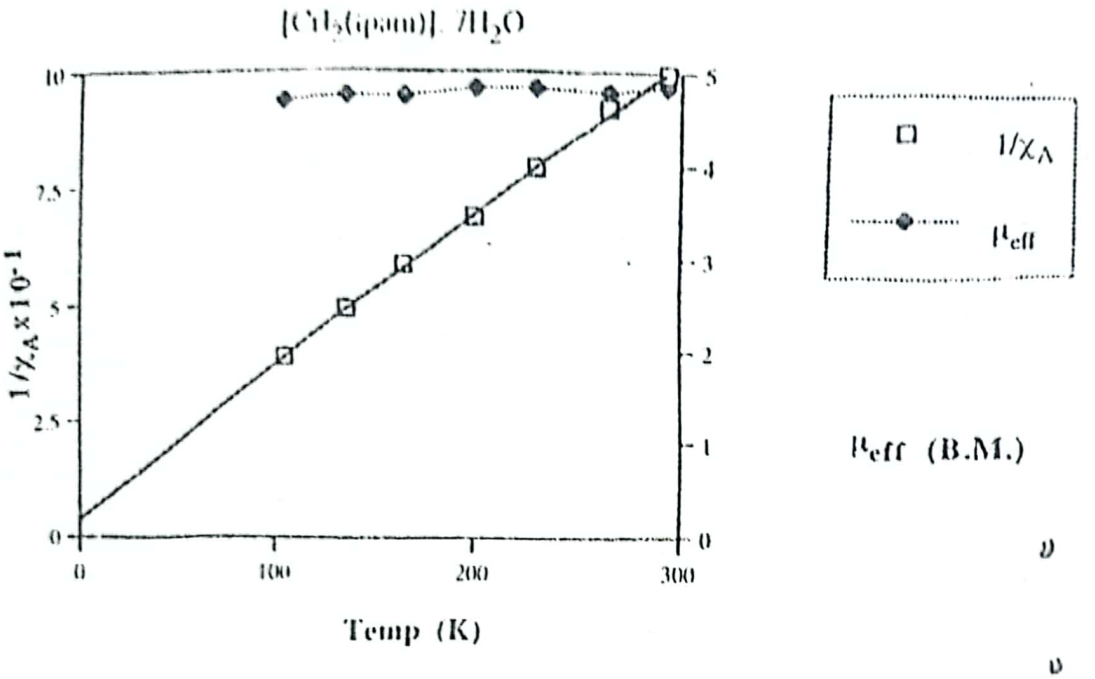
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Figure 3.1


[Cr(tpam)]. 7H2O
1/χA x10-1
Temp (K)
1/χA
μeff
μeff (B.M.)

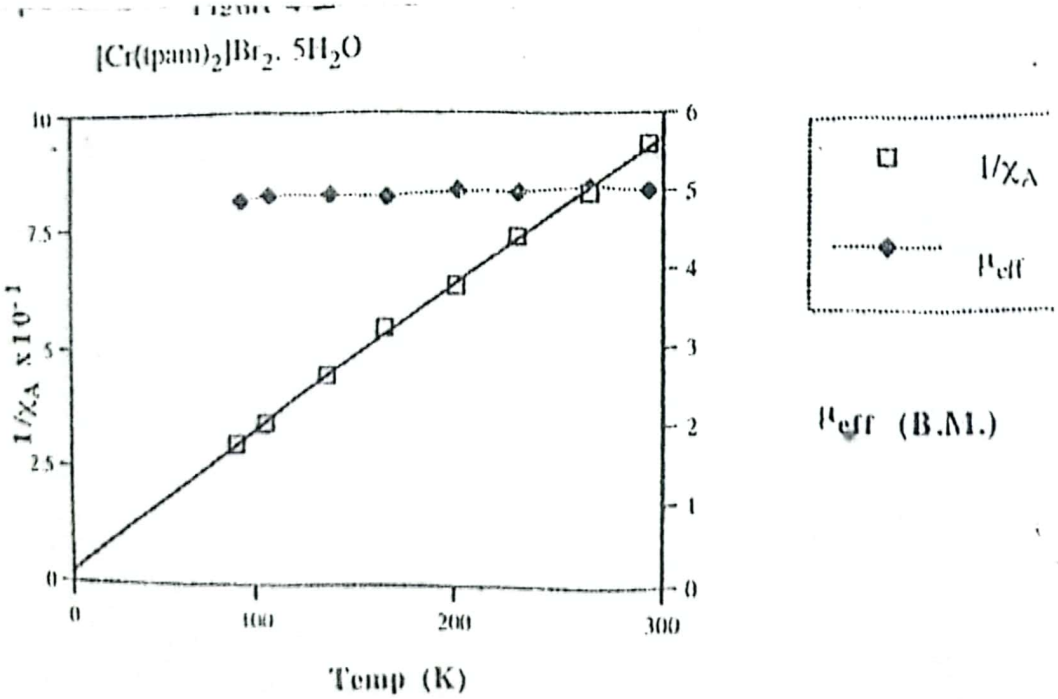

[Cr(tpam)2]Br2. 5H2O
1/χA x10-1
Temp (K)
1/χA
μeff
μeff (B.M.)

Figure 3.1

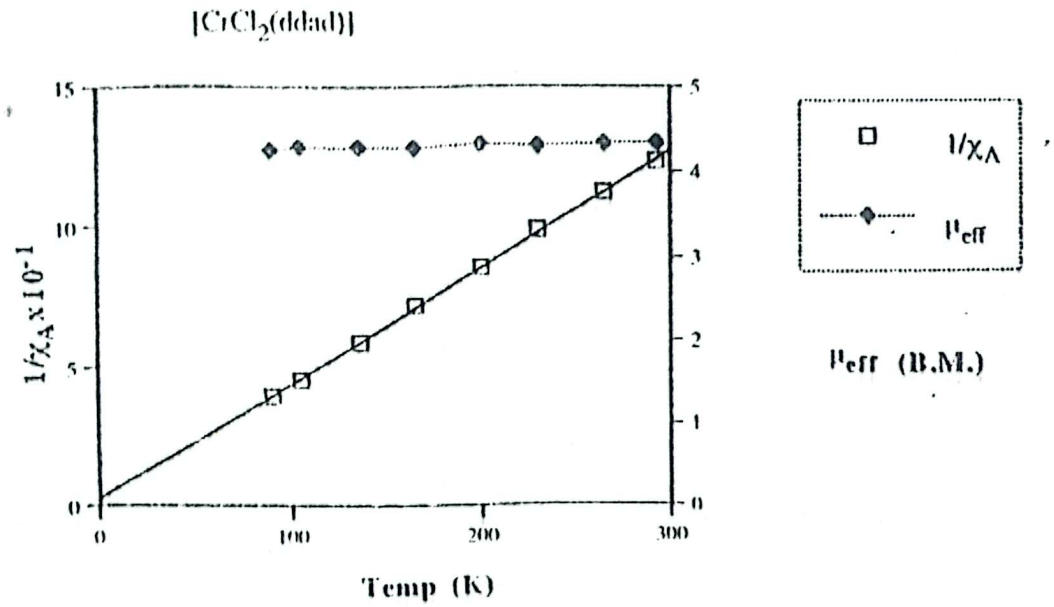


Figure 3.2

