Indian Journal of Chemistry
Vol. 22A, January 1983, pp. 39-42

Coordinating Properties of a Substituted Hydrazine: Bis-complexes of Cobalt(II), Nickel(II) & Copper(II) with Nitroaminoguanidine

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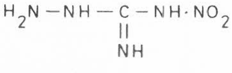
Received 17 *July* 1982; *revised and accepted* 31 *August* 1982

Nitroaminoguanidine (NAG) forms bis-complexes with cobalt(II), nickel(II) and copper(II) salts of the type, $M(NAG)_2X_2.nH_2O$ [M = Co/Ni, X = Cl/Br/I/SCN/NO_3/$\frac{1}{2}SO_4$/ClO_4/BF_4; M = Cu, X = Cl/Br/NO_3/$\frac{1}{2}SO_4$/ClO_4/BF_4; n = 0, 2]. These have been characterised in the solid state through various physicochemical techniques. The ligand, NAG, has been shown to exhibit a neutral N-N function in forming distorted octahedral metallic complexes with different counterions.

The coordination behaviour of substituted hydrazines towards transition metal ions has been reviewed recently[1]. However nitroaminoguanidine (NAG, I) has not, so far, been explored as a complexing ligand. The present paper describes the preparation and characterisation of cobalt(II), nickel(II) and copper(II) complexes with I.



$H_2N-NH-\underset{\underset{NH}{\|}}{C}-NH\cdot NO_2$

(I)

Materials and Methods

Nitroaminoguanidine (NAG) was prepared according to the method of Phillips and Williams[2], m.p. 189-90° (lit. m.p. 190°). (Found: C, 10.09; H, 4.15; N, 58.83. Calc. for $CH_5N_5O_2$: C, 10.15; H, 4.23; N, 58.81%); IR (KBr): 3435(s), 3330(ms), 3220(bs), 1670(bs), 1620(s), 1580(bm), 1290(bm), 1160(s), 1100(ms), 1010(s), 960(w), 900(s) and 785(s) cm^{-1}.

Preparation of metal complexes—$M(NAG)_2X_2.nH_2O$ (M = Co/Ni; X = Cl/Br/I/SCN/$\frac{1}{2}SO_4$/NO_3/ClO_4/BF_4; M = Cu; X = Cl/$\frac{1}{2}SO_4$/NO_3; $n = 0/2$)—A solution of the appropriate hydrated metal(II) salt† (0.005 mol) the appropriate hydrated metal(II) salt† (0.005 mol) was mixed with a hot aq. ethanolic solution of NAG (0.01 mol). The resulting solution (*p*H 3-5) on concentration at a water-bath temperature precipitated the desired compounds when stirred well (Table 1). The complex in each case, was collected on a filter, washed with ethanol and dried in a desiccator over fused calcium chloride.

$Cu(NAG)_2X_2.2H_2O$ (X = Br/ClO_4/BF_4)—An ethanolic solution of the appropriate hydrated copper(II) salt (0.005 mol) was mixed with the solid ligand (0.01 mol). The resulting suspension on stirring for 30 min gave a clear solution which subsequently precipitated out the desired complex species. The complex, in each case, was collected as before.

Equivalent conductance, magnetic susceptibilities and electronic, (both in solid and in solution) and vibrational spectra of the complexes were measured as described earlier[3].

Results and Discussion

The characterisation data of the complexes are in Table 1. All the complexes are highly soluble in water and very slightly soluble in non-donor solvents. The complexes go readily into solution in donor solvents like DMSO, DMF etc. often accompanied with a change in colour of the solution.

Cobalt(II) complexes—The room temperature magnetic moments of cobalt(II) complexes of general formula $Co(NAG)_2X_2.nH_2O$ (X = Cl/Br/I/SCN/NO_3/$\frac{1}{2}SO_4$/ClO_4/BF_4; $n = 0/2$) lie in the range 4.24-4.63 B.M. (Table 1); the values are lower than those (4.8-5.2) observed for octahedral high-spin cobalt(II) species[4], indicating that the Co(II) might have an orbital singlet ground state with distorted octahedral environment[5-7].

The conductances of DMF solutions of $Co(NAG)_2X_2.nH_2O$ (X = Cl/Br/I/SCN/$\frac{1}{2}SO_4$) and $Co(NAG)_2X_2.nH_2O$ (X = NO_3/ClO_4/BF_4) are in the ranges 60.3-65.2 and 132.8-157.3 mho cm^2 mol^{-1} (Table 1) respectively, indicating 1:1 and 1:2 electrolytic nature of the corresponding species[8].

The diffuse reflectance spectra of Co(II) complexes exhibit characteristic absorptions for the transitions ${}^4T_{1g}(F)\rightarrow{}^4T_{2g}$ (ν_1; 9,800-10,500 cm^{-1}) and ${}^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$ (ν_3, 20,600-22,800 cm^{-1}) suggesting an octahedral geometry for the complexes[9]. The ligand field parameters (calculated through known relationship[10]), Dq (1101-1225 cm^{-1}), B (800-941 cm^{-1}) and β (0.82-0.96) provide additional evidence for an

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†Co(II) or Ni(II) thiocyanate solution was prepared by mixing equivalent amounts of metal(II) nitrate and potassium thiocyanate in the same solvent and filtering off the precipitated KNO_3.

Table 1—Analytical and Some Physicochemical Data of the Metal Complexes

Compound	Colour	Found (calc), %			μ_{eff} B.M.	Λ_m ohm $^{-1}$ cm ^{2} mol $^{-1}$	Anion frequences (cm $^{-1}$) with probable assignments
		Metal	N	Anion	(303°K)		
$Co(NAG)_2Cl_2$	Light violet	16.10 (16.03)	38.15 (38.05)	19.25 (19.30)	4.24	65.2	—
$Co(NAG)_2Br_2$	Violet	12.93 (12.91)	30.61 (30.63)	35.13 (35.01)	4.50	62.8	—
$Co(NAG)_2I_2$	Pink	10.62 (10.71)	25.42 (25.40)	46.10 (46.09)	4.63	60.3	—
$Co(NAG)_2(SCN)_2.2H_2O$	Pink	13.25 (13.14)	37.23 (37.42)*	14.28 (14.26)†	4.29	63.6	2115s (νC=N); 810w (νC-8) (N-bonded)
$Co(NAG)_2(NO_3)_2.2H_2O$	Light pink	12.75 (12.90)	36.82 (36.76)*	—	4.52	157.3	1380ms (ν_3); 815w (ν_2) in D_{3h} symmetry
$Co(NAG)_2SO_4.2H_2O$	Pink	13.63 (13.75)	32.59 (32.63)	22.33 (22.38)	4.30	63.1	1100bs (ν_3) in T_d symmetry
$Co(NAG)_2(ClO_4)_2.2H_2O$	Light pink	11.10 (11.09)	26.29 (26.31)	13.38 (13.35)‡	4.51	132.8	1100-1050bs (ν_3) in T_d symmetry
$Co(NAG)_2(BF_4)_2.2H_2O$	Light pink	11.42 (11.65)	27.73 (27.64)	—	4.38	138.8	1090bs (ν_3) in T_d symmetry
$Ni(NAG)_2Cl_2$	Pale blue	15.98 (15.96)	38.13 (38.07)	19.30 (19.32)	2.98	66.9	—
$Ni(NAG)_2Br_2$	Blue violet	12.83 (12.85)	30.67 (30.65)	35.13 (35.02)	3.13	64.6	—
$Ni(NAG)_2I_2$	Blue violet	10.65 (10.66)	25.47 (25.42)	46.20 (46.13)	3.00	62.8	—
$Ni(NAG)_2(SCN)_2$	Violet	14.35 (14.22)	40.56 (40.72)*	15.60 (15.51)†	3.08	76.1	2130vs (νC=N); 810ms (νC−S) (N-bonded)
$Ni(NAG)_2(NO_3)_2.2H_2O$	Pale blue	12.66 (12.85)	36.89 (36.78)*	—	3.09	150.3	1380s (ν_3); 820w (ν_2) in D_{3h} symmetry
$Ni(NAG)_2SO_4.2H_2O$	Light blue	13.72 (13.70)	32.62 (32.66)	22.42 22.40)	3.18	65.5	1100bs (ν_3) in T_d symmetry
$Ni(NAG)_2(ClO_4)_2.2H_2O$	Blue violet	10.90 (11.04)	26.49 (26.32)	13.32 (13.36)‡	2.99	170.3	1110-1070bs (ν_3) in T_d symmetry
$Ni(NAG)_2(BF_4)_2.2H_2O$	Blue violet	11.69 (11.61)	27.80 (27.68)	—	2.88	140.2	1100bs (ν_3) in T_d symmetry
$Cu(NAG)_2Cl_2.2H_2O$	Green	15.52 (15.54)	34.23 (34.27)	17.34 (17.38)	1.78	64.2	—
$Cu(NAG)_2Br_2.2H_2O$	Green	12.78 (12.76)	28.11 (28.14)	32.20 (32.16)	1.50	61.92	—
$Cu(NAG)_2SO_4.2H_2O$	Blue	14.52 (14.65)	32.27 (32.29)	22.18 (22.15)	1.89	**	1100-1180bs (ν_3) in T_d symmetry
$Cu(NAG)_2(NO_3)_2.2H_2O$	Blue	13.71 (13.76)	36.45 (36.40)*	—	1.81	150.3	1380s (ν_3); 825vs (ν_2) in D_{3h} symmetry
$Cu(NAG)_2(ClO_4)_2.2H_2O$	Blue	11.82 (11.84)	26.01 (26.09)	13.26 (13.23)‡	2.17	168.8	1110-1040bs (ν_3) in T_d symmetry
$Cu(NAG)_2(BF_4)_2.2H_2O$	Blue	12.48 (12.43)	27.36 (27.39)	—	1.84	152.3	1100-1020bs (ν_3) in T_d symmetry

*Including the nitrogen of the corresponding anion.
†Percentage of sulphur as $BaSO_4$.
‡Percentage of chlorine as AgCl.
**Molar conductance could not be measured due to low solubility in DMF.

overall pseudo-octahedral geometry for these complexes[11]. The bands appearing near 5000 and 6500 cm $^{-1}$ may be due to ligand overtone mode. No appreciable change is noted when the electronic spectra are recorded in aqueous solutions indicating identical geometry in solid and solution phases. The solution spectra of the complexes are characterised by one principal band in the region 19,420-20,000 cm $^{-1}$, assignable to ν_3 in O_h symmetry. The low values of molar extinctions (1.07-14.81, Table 1) of the principal bands give additional support for an average octahedral environment of the complexes in solution.

Nickel(II) complexes—The room temperature magnetic moments of the bis-nickel(II),

$Ni(NAG)_2X_2.nH_2O$ lie in the range, 2.88-3.18 B.M. (Table 1), expected for six-coordinate spin free nickel(II) complexes[12]. The molar conductance values ($\Lambda_M = 62.8$-170.3 mho cm^2 mol^{-1}; Table 1) in DMF indicate the ionic nature of the complexes at least in DMF[8].

The diffused reflectance and solution electronic spectra of the Ni(II) complexes exhibit two main bands without splitting in the region 8,600-11,400 and 16,000-18,600 cm^{-1}, assignable to ν_1 $[^3A_{2g} \rightarrow {}^3T_{2g}(F)]$ and ν_2 $[^3A_{2g} \rightarrow {}^3T_{1g}(F)]$ transitions respectively in an idealised O_h symmetry[14]. It is noteworthy that 10 *Dq* (ν_1) values of these complexes are comparable to those of the nickel(II) hydrazine complexes (11,000 cm^{-1})[12]. In the complexes $Ni(NAG)_2(SCN)_2$ and $Ni(NAG)_2(NO_3)_2.2H_2O$, the ν_2/ν_1 ratios of 1.63 and 1.58 respectively characterise them as essentially octahedral in the solid state. However, the ν_2/ν_1 values for the other nickel(II) complexes are in the range 1.85-1.89 indicating some degree of tetrahedral distortion in these octahedral species[15]. The weak broad diffused reflectance band between 6,400 and 6,600 cm^{-1} in some of the complexes may arise from a ligand overtone mode. The low values of molar extinction coefficients (2-5) are consistent with an octahedral arrangement of the ligands[16]. The weak shoulders at ~13,000 cm^{-1} in the solution spectra in some of these complexes may be assigned to spin-forbidden transition $^3A_{2g} \rightarrow {}^1E_g(D)$[17].

Copper(II) complexes—The room temperature magnetic moments for majority of the copper(II) complexes lie in the range 1.78-2.17 B.M. (Table 1) indicating distorted octahedral configuration for the species. However, a low magnetic moment value of 1.50 B.M. for $Cu(NAG)_2Br_2.2H_2O$ indicates the complex to be either dimeric or polymeric. The molar conductances ($\Lambda_M = 61.92$-168.8 mho cm^2 mol^{-1}, Table 1) in DMF of the Cu(II) complexes indicate the ionic nature of the complexes in the said solvent.

The diffused reflectance spectra of Cu(II) complexes, $Cu(NAG)_2X_2.2H_2O$, in general, exhibit a broad asymmetric band, in each case, in the region of 15,160-16,260 cm^{-1} indicating distorted octahedral environment for the complexes with a symmetry lower than O_h[18,19]. The electronic spectra in DMF exhibit only one band between 15,800 and 14,710 cm^{-1} which is characteristic for Cu(II) complexes in a distorted octahedral environment; the data also suggest that no gross deviation in stereochemistry of these complexes occurs in solid and solution phases.

IR spectra—The IR spectrum of the ligand in KBr exhibits bands at 3435(s), 3330(ms), and 3220(bs) cm^{-1}, assignable reasonably to νNH or νNH_2. The broad nature of these bands might be due to intra- or intermolecular hydrogen bonding. The bands at 1670(s), 1620(s) and 900(s) cm^{-1} may be assigned respectively to βNH_2, $\nu C=N$ and $\nu N-N$ of the hydrazine moiety.

On complexation with a metal ion, changes that occur in the characteristic absorption of the free ligand are summarised below:

(i) In most of the cases, a small but perceptible negative shift of ($\Delta\nu \sim$ 15-70 cm^{-1}) in νNH or νNH_2 shows that terminal nitrogen of $-NH.NH_2$ group serves as one of the possible coordination sites. This is further supported by the lowering of the stretching frequency ($\Delta\nu = 10-20$ cm^{-1}) attributable to βNH_2 and increase of $\nu N-N$ (~30-50 cm^{-1}) of the hydrazine moiety (as compared to the free ligand)[20-23].

(ii) The conjecture that imino nitrogen (=NH) of the nitroaminoguanidine is another bonding site is substantiated by recognisable lowering of $\nu C=N$ ($\Delta\nu = 10-20$ cm^{-1}) in the metal complexes as compared to the free ligand. It is appropriate here to refer that X-ray[24-26] analyses of the metal biguanide complexes have confirmed the two imino nitrogens (=NH) as the bonding sites. From steric considerations also, it appears that bonding from the terminal nitrogen of the $-NH.NH_2$ group and the imino nitrogen (=NH) to the same metal ion envisages the formation of a five membered ring and this seems to be most reasonable proposition in the metal complexes of nitroaminoguanidine.

(iii) The appearance of a medium strong band around 925-950 cm^{-1} in the IR spectra of $M(NAG)_2X_2.nH_2O$ ($X = NO_3/\frac{1}{2}SO_4/ClO_4/BF_4$) indicates the presence of coordinated water molecules in these complexes[27,28].

The characteristic IR frequencies due to the polyatomic anions are given in Table 1 with probable assignments. The data clearly indicate monodentate nature of thiocyanate[29,30] (N-bonded) whereas nitrate[30], sulphate[31] perchlorate[32] and fluoborate[33,34] retain their ionic character in the metal complexes.

Nitroaminoguanidine (NAG) is, thus, found to exhibit a neutral bidentate N-N function through the hydrazinic nitrogen and iminic nitrogen in forming complexes with a transition metal ion having different counterions.

Acknowledgement

The authors are grateful to Prof. Stanley Livingstone of N.S.W. University, Australia, for kindly providing them with the reflectance spectra of the complexes.

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